

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 202 784 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 25.09.91 (51) Int. Cl.⁵: G03C 1/005

(21) Application number: 86303072.2

(22) Date of filing: 23.04.86

The file contains technical information submitted
after the application was filed and not included in
this specification

(54) Silver halide photographic light-sensitive material.

(30) Priority: 23.04.85 JP 86659/85

(43) Date of publication of application:
26.11.86 Bulletin 86/48

(49) Publication of the grant of the patent:
25.09.91 Bulletin 91/39

(84) Designated Contracting States:
DE FR GB

(56) References cited:
EP-A- 0 147 868
EP-A- 0 152 822
DE-A- 3 310 609
DE-B- 1 169 290

(73) Proprietor: KONICA CORPORATION
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: Matsuzaka, Syoji
255-5 Kamiichibukata-machi
Hachioji-shi Tokyo(JP)
Inventor: Nishiwaki, Shu
c/o Konishiroku Photo Industry Co. Ltd.
No. 1 Sakura Machi Hino City Tokyo 191(JP)
Inventor: Suda, Yoshihiko
6-5-2 Tamadalra
No. 313 Hino-shi Tokyo(JP)
Inventor: Kamio, Takashi
2-5-19 Owada-machi
Hachioji-shi Tokyo(JP)
Inventor: Terao, Toshimi
c/o Konishiroku Photo Industry Co. Ltd.
No. 1 Sakura Machi Hino City Tokyo 191(JP)
Inventor: Iijima, Toshifumi
2-13-9 Shin-machi
Kokubunji-shi Tokyo(JP)

(74) Representative: Ellis-Jones, Patrick George
Armstrong et al
J.A. KEMP & CO, 14 South Square Gray's Inn
London WC1R 5EU(GB)

EP 0 202 784 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to a silver halide photographic light sensitive material containing negative type silver halide grains each having an inner core substantially comprising silver bromide or silver iodobromide surrounded by a plurality of outer shells each substantially composed of silver bromide or silver iodobromide.

In recent years, as there have been more stringent requirements for silver halide emulsions for photographic use, the demands for high-level photographic characteristics such as a high-speed, an excellent graininess, a high sharpness, a low fog-density, and a sufficiently wide exposure range have increased.

High-speed emulsions such as a silver iodobromide emulsion containing silver iodide in an amount of from 0 to 10 mol% of the emulsion to satisfy the above-mentioned requirements are known. As regards the methods of preparing the above-mentioned emulsions, the well-known methods include, for example, an ammonia method, a neutral method, an acid method in which the conditions of pH and pAg values are controlled, and a precipitation method such as a single-jet or double-jet method.

Based upon the above-mentioned prior art research has been carried out with the intention of improving the sensitivity and graininess of light-sensitive materials and, further, achieving both high sharpness and low fog. A silver iodobromide emulsion which is provided by the invention has been studied so as to control not only the crystal habits and grain distribution but also the iodide content distribution in an individual silver halide grain.

To achieve the photographic characteristics including, for example, a high speed, excellent graininess, high sharpness or low fog density, the most conventional process is to improve the quantum efficiency of the silver halide used. For this purpose, studies have been made of solid state physics and the like.

There has been research in which the above-mentioned quantum efficiency was theoretically computed and the influence on a graininess distribution was also studied. Such research is described in, for example, the preprints of 1980 Tokyo Symposium on Photographic Progress, titled 'Interactions Between Light and Materials', p. 91. This research predicts that a quantum efficiency could effectively be improved if a monodispersed emulsion may be prepared by narrowing a grain distribution. Further, in the so-called chemical sensitization process for sensitizing a silver halide emulsion (This process will be described in detail later.), it may be reasonably presumed that a monodispersed emulsion may also be advantageous to effectively make a light-sensitive material highly sensitive whilst maintaining a low fog level.

To prepare such a monodispersed emulsion on an industrial scale, it is desired, as described in Japanese Patent Publication Open to Public Inspection (hereinafter called Japanese Patent O.P.I. Publication) No. 48521/1979, to apply both of the theoretically predetermined conditions of the feeding rate controls of silver ions and halide ions to be fed into a reaction system and the satisfactory conditions of the agitation thereof to the preparation process under the strict controls of the pAg and pH values of the emulsion. When a silver halide emulsion is prepared under the above-mentioned conditions, it is in either the cubic, octahedral or tetradecahedral crystal form. Such an emulsion comprises the so-called normal crystal grains each having both of the (100) and (111) planes in various ratios. It is well-known that a high sensitization may be achieved by making use of the above-mentioned normal crystal grains.

It is known that the silver halide emulsions suitably used in high speed photographic films include a silver iodobromide emulsion comprising polydispersed type twinned crystal grains.

Also, silver iodobromide emulsions each containing tabular shaped twinned crystal grains are disclosed in, for example, Japanese Patent O.P.I. Publication No. 113927/1983 and others.

Additionally Japanese Patent O.P.I. Publication No. 22408/1978; Japanese Patent Examined Publication No. 13162/1988; 'Journal of Photographic Science', No. 24, p. 198, 1978; and the like each describe, respectively, that development activity is increased or high sensitization is realized by making use of multilayered type silver halide grains applied with a plurality of shells around the inner cores of the grains.

Furthermore, West German Patent No. 2,932,650; Japanese Patent O.P.I. Publication Nos. 2417/1976, 17436/1976 and 11927/1977; and the like describe the respective silver halide grains each provided with a covering layer by a halogen substitution so as to serve as the outermost layer of the silver halide grain. These silver halide grains are not suitable for a negative type emulsion, because the fixing time is reduced. Also, development may be thereby inhibited, so that satisfactory sensitivity may not be obtained.

There is also well-known positive type (i.e., an internal latent image type) silver halide grains each provided outside the inner core thereof with a plurality of covering layers prepared through a halogen substitution, such as those described in, for example, U.S. Patent Nos. 2,592,250 and 4,075,020; and Japanese Patent O.P.I. Publication No. 127549/1980. These silver halide grains are often used in an internal latent image type direct positive light-sensitive material such as those for diffusion transferring use.

However, they cannot be used at all in any negative type emulsion to which the invention is directed, because the internal sensitivity thereof is excessively high.

There is a further silver halide grain provided on the inner core thereof with shells, as described above, and in which various iodide contents of the respective layers thereof are taken into account. This type of grains are described in, for example, Japanese Patent O.P.I. Publication nos. 181037/1983, 35726/1985 and 116647/1984.

DE-A-3310609 discloses a silver halide photographic material comprising silver halide grains provided with iodobromide grains having an average iodide content of at least 12 mol%. The grains comprise at least 3 different iodobromide phases, each having a different iodide content. Whilst the precise relative iodide content of the layers is not critical, the external phase preferably has an average iodide content of between 5 and 13 mol percent of the average content of the entire grain; the second phase preferably contains between 15 and 25 mol percent and the innermost phase preferably has a content of between 30 and 70 mol percent.

In the field of silver halide photographic light-sensitive materials, color light-sensitive materials each having an ISO speed of 1000 or over have recently been introduced. It is, however, usual that as such a light-sensitive material shows improved sensitivity, it deteriorates in terms of graininess and sharpness.

Accordingly, such a high speed light-sensitive material has, so far been unsatisfactory for the consumers who want to admire a good photograph because its image quality is not as good as a conventional light-sensitive material. Therefore, a high-speed negative type light-sensitive material excellent in graininess and image sharpness is required.

For astronomical photography, indoor photography, sport photography and the like, a further high-speed negative type light-sensitive material is particularly called for.

The present invention seeks to provide a negative type silver halide photographic light-sensitive material which is high in sensitivity, excellent in the correlation between sensitivity and fog, wide in the exposure range, and excellent in both graininess and image sharpness. This may be accomplished, according to the present invention, by a negative type silver halide photographic material comprising silver halide grains of a core-shell structure which consists of an inner core essentially consisting of silver bromide or silver iodobromide and a plurality of shells, essentially consisting of silver bromide or silver iodobromide, wherein each of the silver halide grains comprises (a) an outermost shell containing silver iodide of 0 to 10 mol%, (b) a highly iodide-containing shell provided inside the outermost shell, of which silver iodide content is from 6 to 40 mol% and is at least 6 mol% higher than that of the outermost shell, and (c) an intermediate shell provided between the shells (a) and (b) the silver iodide content of the intermediate shell being at least 3 mol% higher than that of the outermost shell, and at least 3 mol% lower than that of the high iodide-containing shell.

In the silver halide composition of the silver halide grains relating to the invention, the expression, 'substantially comprising ----', means that the above-mentioned silver halide grains are allowed to contain such a silver halide other than silver bromide or silver iodide as silver chloride and, more particularly, means that the content thereof is desirably not more than 1 mol% if it is silver chloride, provided that the content thereof does not disturb the advantages of the invention.

The special features of the photographic light-sensitive materials of the invention may be summarized as given below:

- (1) A high-speed, a wide exposure range and an excellent graininess (as compared with non-core/shell type emulsions) may be obtained by making use of emulsion containing core/shell type silver halide grains each surrounding highly iodide-containing shells;
- (2) The property of high-speed may be further improved by interposing an intermediate shell between the highly iodide-containing shell and the outermost low iodide-containing shell, provided that the iodide content of the intermediate shell is in a range between that of the low iodide-containing shell and that of the outermost shell;
- (3) The iodide content of the highly iodide-containing shell should be from 6 to 40 mol% and is at least 6 mol% higher than the outermost shell. If the iodide content thereof is less than 6 mol% (or, if the difference in iodide content is less than 6 mol%, the sensitivity of the light-sensitive material is reduced. In addition, if it exceeds 40 mol%, the light-sensitive material is polydispersed. Therefore, having regard to the sensitivity and the image sharpness it is necessary that the iodide content of a highly iodide-containing shell does not exceed 40 mol%.
- (4) The difference between the iodide content of an intermediate shell and that of the outermost shell, or between the intermediate shell and that of a highly iodide-containing shell is not less than 3 mol%. Because, if the difference is too small, the advantageous properties of the intermediate shell are reduced. (i.e., the sensitivity of a light-sensitive material is reduced.) From the viewpoint of that the

advantages of the intermediate shell (in sensitivity, monodispersibility, fog-sensitivity correlation and image sharpness) are effectively induced, it is preferred to specify the upper limit of the difference between these iodide contents up to 35 mol%.

(5) When the iodide content of the whole silver halide grains is in excess, the developability and sensitivity of the light-sensitive material tend to be reduced, the gradation tends to be too hard and the exposure range narrowed and further the graininess worsened. It is, therefore, preferred to choose an iodide content within the aforementioned range.

(6) A monodispersed emulsion is superior to a polydispersed emulsion in sensitivity, sharpness and has an improved correlation between fogginess and sensitivity. In polydispersed emulsions, it is difficult to achieve an ideal core/shell structure, because the shell-forming reactions thereof are not uniform; fine grains are present therein so as to deteriorate the sharpness; the sensitivity thereof is lowered and the correlation between fogginess and sensitivity tends to deteriorate, because the optimum conditions for chemically sensitizing the emulsion after the grains thereof were formed depend upon the individual grains. For these reasons monodispersed emulsions are preferred.

(7) When a light-sensitive material is multilayered, the multilayer-sensitivity thereof is inferior to the monolayer-sensitivity. (This phenomenon is called an interlayer desensitization effect.) The emulsions of the invention are not only high in monolayer sensitivity, but are also hardly affected by the above-mentioned interlayer desensitization effect. Therefore, the emulsions of the invention may effectively be used in such multilayered color light-sensitive materials.

Preferred compositions according to the invention satisfy the following criteria:

The shells have an iodide content as follows:

lh : An iodide content of a highly iodide-containing shell (mol%);

lm : An iodide content of an intermediate shell (mol%); and

ll : An iodide content of an outermost shell (mol%);

It is preferred that $\Delta l = lh - ll > 8$ mol%, $\Delta lh = lh - lm > 4$ mol% and $\Delta ll = lm - ll > 4$ mol%; and it is further preferred for $\Delta l > 10$ mol%, $\Delta lh > 4$ mol% and $\Delta ll > 4$ mol%. {Refer to the above-mentioned item (4)}; wherein ll is preferably from 0 to 5 mol% and, more preferably, from 0 to 2 mol% and, further preferably, from 0 to 1 mol%; and lh is from 6 to 40 mol% and, preferably, from 10 to 40 mol%. {Refer to the above-mentioned item (3)}.

The volume of the outermost shell preferably comprises from 4 to 70% of the whole grain and, more preferably, from 10 to 50% thereof. The volume of the highly iodide-containing shell preferably comprises from 10 to 80% of a whole grain and, more preferably, from 20 to 50% and, further preferably, from 20 to 45% thereof. The volume of the intermediate shell preferably comprises from 5 to 60% of a whole grain and, more preferably, from 20 to 55% thereof. The highly iodide-containing shell may comprise at least one part of an inner core and, more preferably, a separate inner shell is present inside the highly iodide-containing shell.

The iodide content of the inner shell is preferably from 0 to 40 mol% and, more preferably, from 0 to 10 mol% and, further preferably, from 0 to 6 mol%. The grain size of the inner core is preferably from 0.05 to 0.8 μm and, more preferably, from 0.05 to 0.4 μm .

In the distinctive features described in the above-mentioned item (5), the iodide content of the whole grain is preferably from 1 to 20 mol% and, more preferably, from 1 to 15 mol% and, further preferably, from 2 to 12 mol%. In the distinctive features described in the above-mentioned item (6), the grain size distribution is allowed to be either one of the polydisperse type and the monodisperse type. However, the variation coefficient of such grain size distribution is preferably not more than 20% in a monodispersed emulsion and, more preferably, not more than 15%. Such a variation coefficient will be defined as follows to measure a monodispersibility:

$$\text{Variation coefficient (\%)} = \frac{\text{Standard deviation of grain size}}{\text{Average grain size}} \times 100$$

As for a multilayered color light-sensitive material having the features mentioned in the item (7), it is desired that the multilayered arrangement is made of not less than three emulsion layers comprising three kinds of light-sensitive layers; a blue-sensitive layer, a red-sensitive layer and a green-sensitive layer; and at least one emulsion layer thereof contains the silver halide grains relating to the invention or the above-mentioned desirable silver halide grains.

The grain size of a silver halide grain (which is defined as a length of one side of a cube having the same volume as that of the silver halide grain) is preferably from 0.1 to 3.0 μm ; and the configuration thereof may be, for example, an octahedron, a cube, a sphere, or a flat plate and, most preferably, an octahedron.

The layer arrangements of the silver halide grains of the invention will further be described below:

5 As mentioned above, the inner shell may be the highly iodide-containing shell, or there may be both an inner shell and a highly iodide-containing shell. The inner shell and the highly iodide-containing shell, the highly iodide-containing shell and the intermediate shell, and the intermediate shell and the outermost shell may be adjacent to each other; or, optionally another shell comprising at least one layer having an arbitrary composition (hereinafter called an arbitrary shell) may be interposed between the above-mentioned shells.

10 The above-mentioned arbitrary shell may suitably be a monolayered shell having a uniform composition, a plurality of shells each having a uniform composition with a stepwise change in composition from shell to shell, a continuous shell which changes its composition gradually in its arbitrary shell, and the combination thereof. The above-mentioned highly iodide-containing shell and intermediate shell may be used together as a pair or a plurality of layers may be employed.

15 Examples of the layer arrangements of the silver halide grains relating to the invention are as follows: iodide content will be represented by I. Subscripts denote the order of shells.

1. 3-layer structure of an inner core a highly iodide-containing shell:

	iodide content	Shell diameter
Core (3rd) (Inner core = Highly iodide-containing shell)		
	$I_3 - I_2 > 3 \text{ mol\%}$	$I_3 = 15 \text{ mol\%}$ 1.2 μm
2nd shell (Intermediate shell)		
	$I_2 - I_1 > 3 \text{ mol\%}$	$I_2 = 5 \text{ mol\%}$ 1.4 μm
1st shell (Outermost shell)		
	$I_1 = 0-10 \text{ mol\%}$	$I_1 = 0.5 \text{ mol\%}$ 1.6 μm

2. 6-layer structure interposing the 4th and 5th shells each having an arbitrary composition between an inner core and a highly iodide-containing shell:

	iodid content	Shell diam ter
5	Cor (6th) (Inner cor)	
	Arbitrariness $I_1 = 4.0 \text{ mol\%}$	$0.1 \mu\text{m}$
	5th shell (Arbitrary shell)	
10	Arbitrariness $I_1 = 2.0 \text{ mol\%}$	$0.27 \mu\text{m}$
	4th shell (Arbitrary shell)	
15	Arbitrariness $I_1 = 2.6 \text{ mol\%}$	$0.8 \mu\text{m}$
	3rd shell (Highly iodide-containing shell)	
	$I_1 - I_2 > 3 \text{ mol\%}$ $I_1 = 15.0 \text{ mol\%}$	$1.12 \mu\text{m}$
20	2nd shell (Intermediate shell)	
	$I_1 - I_2 > 3 \text{ mol\%}$ $I_1 = 5.0 \text{ mol\%}$	$1.44 \mu\text{m}$
25	1st shell (Outermost shell)	
	$I_1 = 0 \sim 10 \text{ mol\%}$ $I_1 = 0.5 \text{ mol\%}$	$1.6 \mu\text{m}$

30 3. 7-layer structure interposing the 5th and 6th shells between an inner shell and a highly iodide-containing shell and also interposing a 2-layered intermediate shell between the outermost shell and the highly iodide-containing shell:

35

40

45

50

55

	i dide content	Shell diamet r
5	7th shell (Inner core)	
	$I_7 = 4 \text{ mol\%}$	$0.10 \mu\text{m}$
	6th shell (Arbitrary shell)	
10	Arbitrariness $I_6 = 2 \text{ mol\%}$	$0.27 \mu\text{m}$
	5th shell (Arbitrary shell)	
	Arbitrariness $I_5 = 8 \text{ mol\%}$	$0.8 \mu\text{m}$
15	4th shell (Highly iodide-containing shell)	
	$I_4 - I_3 > 3 \text{ mol\%}$ $I_4 = 15 \text{ mol\%}$	$1.12 \mu\text{m}$
20	3rd shell (Intermediate shell)	
	$I_3 - I_2 > 3 \text{ mol\%}$ $I_3 = 8 \text{ mol\%}$	$1.24 \mu\text{m}$
	$I_4 - I_3 > 3 \text{ mol}$	
25	2nd shell (Intermediate shell)	
	$I_2 - I_1 > 3 \text{ mol\%}$ $I_2 = 4 \text{ mol\%}$	$1.44 \mu\text{m}$
30	$I_4 - I_3 > 3 \text{ mol\%}$	
	1st shell (Outermost shell)	
35	$I_1 = 0-10 \text{ mol\%}$ $I_1 = 0.5 \text{ mol\%}$	$1.6 \mu\text{m}$

4. 8-layer structure interposing respectively the arbitrary 6th and 7th shells between an inner shell and a highly iodide-containing shell, an arbitrary single-layered shell (4th shell) between a highly iodide-containing shell (5th shell) and an intermediate shell (3rd shell), and an arbitrary single-layered shell (2nd shell) between the intermediate shell (3rd shell) and the outermost shell:

	iodide content	Shell diameter
5	8th shell (Inner core)	
	Arbitrariness $I_8 = 4 \text{ mol\%}$	0.10 μm
	7th shell (Arbitrary shell)	
10	Arbitrariness $I_7 = 2 \text{ mol\%}$	0.27 μm
	6th shell (Arbitrary shell)	
15	Arbitrariness $I_6 = 4 \text{ mol\%}$	0.8 μm
	5th shell (Highly iodide-containing shell)	
	$I_5 - I_4 > 3 \text{ mol\%}$ $I_5 = 15 \text{ mol\%}$	1.12 μm
20	4th shell (Arbitrary shell)	
	Arbitrariness $I_4 = 9 \text{ mol\%}$	1.24 μm
	3rd shell (Intermediate shell)	
25	$I_3 - I_2 > 3 \text{ mol\%}$ $I_3 = 5 \text{ mol\%}$	1.44 μm
	2nd shell (Arbitrary shell)	
30	Arbitrariness $I_2 = 4.5 \text{ mol\%}$	1.30 μm
	1st shell (Outermost shell)	
35	$I_1 = 0 \sim 10 \text{ mol\%}$ $I_1 = 2 \text{ mol\%}$	1.6 μm

5. Structure having a plurality of highly iodide-containing shells:

	iodide content	Shell diameter
40	6th shell (Inner core)	
	Arbitrariness $I_6 = 4 \text{ mol\%}$	0.10 μm
45	5th shell (Highly iodide-containing shell)	
	$I_5 - I_4 > 3 \text{ mol\%}$ $I_5 = 15 \text{ mol\%}$	0.27 μm
50	$I_5 - I_4 > 6 \text{ mol\%}$	
	4th shell (Arbitrary shell)	
	Arbitrariness $I_4 = 5 \text{ mol\%}$	0.80 μm
55	3rd shell (Highly iodide-containing shell)	

$I_1 - I_2 > 3 \text{ mol\%}$ $I_1 = 15 \text{ mol\%}$ $1.12 \mu\text{m}$

$I_1 - I_2 > 6 \text{ mol\%}$

5 2nd shell (Intermediate shell)

$I_1 - I_2 > 3 \text{ mol\%}$ $I_1 = 5 \text{ mol\%}$ $1.44 \mu\text{m}$

10 1st shell (Outermost shell)

$I_1 = 0-10 \text{ mol\%}$ $I_1 = 0.3 \text{ mol\%}$ $1.60 \mu\text{m}$

The inner cores of the silver halide grains of the invention can be prepared by a process as described in, for example, P. Glafkides, 'Chimie et Physique Photographique', published by Paul Montel, 1967; G.F. Duffin, 'Photographic Emulsion Chemistry', published by The Focal Press, 1966; V.L. Zelikman et al, 'Making and Coating Photographic Emulsion', published by The Focal Press, 1964; Such processes typically include an acid method process, a neutral method process, and an ammonia method process. Further, a single-jet precipitation process, a double-jet precipitation process or the combination thereof may also be applied to cause the reaction between a soluble silver salt and a soluble halide.

In addition, the reverse precipitation process may be employed in which grains may be formed in presence of silver ions in excess. The controlled double-jet precipitation process, a version of the double-jet precipitation processes, may also be applied for keeping a pAg value of a silver halide produced in a liquid phase. According to this process, a silver halide emulsion regular in crystal form and nearly uniform in grain size may be prepared.

It is also possible to use a mixture of two or more kinds of silver halide emulsions each prepared separately, and in this case a double-jet precipitation process or a controlled double-jet precipitation process is preferably used.

The A pAg value varies in accordance with the reaction temperature and the kinds of silver halide solvents in the preparation of an inner core, and is preferably from 2 to 11. It is also preferred to use a silver halide solvent, because the grain-forming time may be reduced. A silver halide solvent such as ammonia or thioether may be used.

Inner cores may be used in a flat plate, sphere or twinned crystal system and also in the form of an octahedron, cube, tetracahedron or the mixed forms thereof.

In order to prepare grains of uniform size, it is preferred to grow up grains rapidly within the critical saturation limit, in a process such as that described in, for example, British Patent No. 1,535,016; and Japanese Patent Examined Publication Nos. 36890/1973 and 16364/1977, in which the respective rates of addition of silver nitrate and an aqueous solution of a halogenated alkali are adjusted according to the growth rate of the grains; or in such a process as described in, for example, 4,242,445 and Japanese Patent O.P.I. Publication No. 158124/1980, in which the concentration of an aqueous solution is adjusted. The above-mentioned processes may also advantageously be used to introduce arbitrary shells, highly iodide-containing shells, intermediate shells or the outermost shells, because new renucleation will not occur and each silver halide grain is uniformly coated in these processes.

In the invention, if necessary, a single shell or a plurality of arbitrary shells may be interposed between the highly iodide-containing shell comprising silver halide grains and the intermediate shell. Such highly iodide-containing shells may be provided by a process including a desalting step, if necessary, applied to the resultant inner shell or the inner shell provided with an arbitrary shell and an ordinary halogen substitution process a silver halide coating process or the like is then performed.

The halogen substitution process may be performed for example, such that, after an inner core is formed, an aqueous solution mainly comprising an iodide compound (preferably, potassium iodide), which is preferably not higher than 10% in concentration, is added. This processes are more particularly described in, for example, U.S. Patent Nos. 2,592,250 and 4,075,020; Japanese Patent O.P.I. Publication No. 127549/1980; and the like. To decrease the difference in an iodide distribution between the grains of the highly iodide-containing shell, it is preferable, in this process, to adjust the concentration of the aqueous iodide compound solution to 10^{-2} mol\% or lower and then to add the solution over a period of at least ten minutes.

The processes for providing a coating of a silver halide an inner core includ , for example, the double-jet precipitation process and controlled double-jet precipitation process, in which, in each cas , an aqueous

halide solution and an aqueous silver nitrate solution are simultaneously added. More specifically, the processes are described in detail in, for example, Japanese Patent O.P.I. Publication Nos. 22408/1978 and 14829/1983; Japanese Patent Examined Publication No. 13162/1988; 'Journal of Photographic Science', No. 24, 198, 1976; and the like.

5 When the highly iodide-containing shell is formed, the pAg value is varied in accordance with the reaction temperature and the nature and the amount of silver halide solvents used. The same conditions as those for the case of the above-mentioned inner core are appropriate to this case. When using ammonia as a solvent, a pAg value of from 7 to 11 is preferred.

10 For the preparation of the highly iodide-containing shell, a double-jet precipitation process or a controlled double-jet precipitation process is preferred.

The intermediate shells, of the silver halide grains of the invention may be prepared such that a highly iodide-containing shell is arranged onto the surface of a grain containing the above-mentioned highly iodide-containing shells and the inner shells, or, if required, the highly iodide-containing shell is provided thereon with a single or plurality of arbitrary shells and, to the outside of the above-mentioned grain, a silver halide a
15 halogen composition different from those of the highly iodide-containing shells is further coated in a double-jet or controlled double-jet precipitation process or the like.

The aforementioned process for preparing highly iodide-containing shell may similarly serve as the above-mentioned processes.

20 The outermost shell of the silver halide grains of the invention may be provided in such a manner that an intermediate shell is provided to the surface of a grain containing the above-mentioned intermediate shells, the highly iodide-containing shells and the inner core or, if required, the intermediate shell provided thereon with a single or plurality of arbitrary shells and, to the outside of the above-mentioned grain, a silver halide having a halogen composition different from those of the highly iodide-containing shells and the intermediate shells is further coated in a double-jet or controlled double-jet precipitation process or the like.

25 The aforementioned highly iodide-containing shell providing process is similarly applied to serve as the above-mentioned processes.

Any number of arbitrary shells may optionally be interposed if required, between the inner core and the highly iodide-containing shell, and/or between the highly iodide-containing shell and an intermediate shell, and/or the intermediate shell and the outermost shell.

30 The above-mentioned arbitrary shells may be prepared by the same processes as employed to prepare the aforementioned highly iodide-containing shell. When trying to provide a shell adjacent to an inner core, a highly iodide-containing shell, an outermost shell or arbitrary shells provided to the respective positions, an ordinary desalting process may be performed to prepare the adjacent shell. Alternatively if required, such shells may be continuously formed without carrying out any desalting.

35 Structural characteristics of the silver halide grains of the invention such as the iodide content of each coated shell of the silver halide grains may be determined by such methods as that described in, for example, J.I. Goldstein and D.B. Williams, 'X-Ray Analyses in TEM/ATEM', Scanning Electron Microscopy, 1977, vol. 1, LIT Research Institute, p. 651, March, 1977; 'Annual Meeting of SPSTJ '84', p 49-51 (1984); 'The International East-West Symposium on the Factors Influencing Photographic Sensitivity (1984)', c-60-c-63 (1984); Japanese Patent O.P.I. Publication No. 143331/1985 and Japanese Patent O.P.I. Publication No. 143332.

40 It is possible to remove an excessive halide or a salt or compound such as a nitrate, ammonia and the like produced as a by-product from the dispersion-medium of the grains which are the final products obtained after the outermost shell of the invention was formed. The suitable methods of removing the above-mentioned materials typically include, for example, a noodle washing method usually applied to an ordinary type emulsion; a dialysis method; a sedimentation method utilizing an inorganic salt, an anionic surfactant, such an anionic polymer as a polystyrene sulfonic acid, or such a gelatin derivative as an acylated or carbamoylated gelatin; and a flocculation method.

45 The core/shell type silver halide grains of the invention can be optically sensitized to a desired wavelength region, and there is no special limitation to the optical sensitization methods. The grains may be optically sensitized by making use, independently or in combination, of an optical sensitizer such as cyanine or merocyanine dyes suitably including, for example, zero-methine, monomethine, dimethine, and trimethine. A combination of spectrally sensitizing dyes is often used particularly for a supersensitization. An emulsion may contain, as well as the above-mentioned spectrally sensitizing dyes, a dye having no
55 spectrally sensitizing characteristic in itself or a substance substantially incapable of absorbing any visible rays off light but capable of displaying super-sensitizing characteristics. These techniques are described in, for example, U.S. Patent Nos. 2,688,545, 2,912,329, 3,397,060, 3,615,535 and 3,628,964; British Patent Nos. 1,195,320, 1,242,588 and 1,293,862; West German (OLS) Patent Nos. 2,030,326 and 2,121,780; Japanese

Patent Examined Publication Nos. 4936/1968 and 14030/1969; R s arch Disclosure, vol. 176, No. 17643, published in Dec., 1978, p. 23, Paragraph IV, Item J; and the like. The above-mentioned techniques may be optionally selected according to a wavelength region, sensitivity and the like to which a sensitization is to be applied and, additionally in accordance with the purpose and use of a light-sensitive material.

5 The core/shell type silver halide crystals of the invention may also be treated by various chemical sensitization processes applicable to ordinary type emulsions.

The chemical sensitization may be carried out by a process such as that described in, for example, H. Frieser, 'Die Grundlagen der Photographische Prozesse mit Silberhalogeniden', Akademische Verlagsgesellschaft, 1968, pp. 675-34. Namely, there may be used, independently or in combination, a sulfur sensitization process employing a compound or active gelatin containing sulfur capable of reacting with silver ions; a reduction sensitization process employing a reducible substance; a noble-metal sensitization process employing gold and other noble-metal compounds; and the like. As for the sulfur sensitizers, a thiosulfate, a thiourea, a thiazole, a rhodanine and other compounds may be used. They typically include those described in U.S. Patent Nos. 1,574,944, 2,410,589, 2,278,947, 2,728,668, 3,656,955, 4,032,928 and 4,067,740. As for the reduction sensitizers, a stannous salt, an amine, a hydrazine derivative, a formamidline sulfonic acid, a silane compound may suitably be used. They typically include those described in U.S. Patent Nos. 2,487,850, 2,419,974, 2,518,698, 2,983,609, 2,983,610, 2,694,637, 3,930,867 and 4,054,458. For the noble-metal sensitization, a gold complex salt and the metal complex salts of the VIII group of the periodic table, such as platinum, iridium, and palladium may suitably be used. They typically include those described in U.S. Patent Nos. 2,399,083 and 2,448,080; British Patent No. 618,061; and the like.

The silver halide grains of the invention may be treated by a combination of two or more of the above-mentioned chemical sensitization processes.

The amount of silver to be coated is not limited but is preferably in the range of from 1000mg/m² to 15000mg/m² and, more preferably, from 2000mg/m² to 10000mg/m².

25 The light-sensitive layers each containing the above-mentioned grains may be present on both sides of a support.

When forming each of the shells of the core/shell type emulsion of the invention, various kinds of dopants may be doped. The inner dopants include, for example, silver, sulfur, iridium, gold, platinum, osmium, rhodium, tellurium, selenium, cadmium, zinc, lead, thallium, iron, antimony, bismuth, and arsenic.

30 To dope the above-mentioned dopants, the water-soluble salts or complex salts thereof may be used in combination with the dopants when forming each of the shells.

For the binders to be used in the core/shell type silver halide grains of the invention, or the dispersion medium to be used in the manufacturing process thereof, a hydrophilic colloid ordinarily used in a silver halide emulsion may also be used. For the hydrophilic colloids mentioned above, examples include gelatin, 35 whether lime- or acid-treated and also the following; namely, a gelatin derivative including, for example, those prepared through a reaction of gelatin on any one of an aromatic sulfonyl chloride, acid chloride, acid anhydride, isocyanate or 1,4-diketone, such as described in U.S. Patent No. 2,614,928; a gelatin derivative prepared by a reaction of gelatin on a trimellitic acid anhydride, such as described in U.S. Patent No. 3,118,766; a gelatin derivative prepared by a reaction of gelatin on an organic acid having an active halogen, such as described in Japanese Patent Examined Publication No. 5514/1964; a gelatin derivative prepared by a reaction of gelatin on an aromatic glycidyl ether, such as described in Japanese Patent Examined Publication No. 26845/1967; a gelatin derivative prepared by a reaction of gelatin on a maleimide, maleamic acid or unsaturated aliphatic diamide and the like, such as described in U.S. Patent No. 3,186,846; a sulfoalkylated gelatin described in British Patent No. 1,033,189; a polyoxyalkylene derivative of a gelatin described in U.S. Patent No. 3,312,553; a graft gelatin polymer with acrylic acid, methacrylic acid or the esters thereof with a mono- or poly-valent alcohol; a graft gelatin polymer with an amide, acrylonitrile or methacrylonitrile, styrene, or other vinyl monomers used independently or in combination; a synthetic hydrophilic high molecular substance including, for example, a homopolymer comprising a monomer such as vinyl alcohol, N-vinylpyrrolidone, hydroxyalkyl (metha)acrylate, (metha)acrylamide, or N-substituted (metha)acrylamide, or the copolymers prepared with each other homopolymers mentioned above, a copolymer prepared with either one of the above-mentioned substances and, for example maleic acid anhydride or maleamic acid; a natural hydrophilic high molecular substance other than gelatin including, for example, an independent or a combination of casein, agar and an alginic polysaccharide.

50 The silver halide photographic emulsions each containing the core/shell type silver halide grains of the invention may further contain various kinds of additives ordinary used according to the purposes.

The above-mentioned additives include, for example, a stabilizer and an antifoggant such as an azole or an imidazole, e.g., a benzothiazolium salt, a nitroindazole, a nitrobenzimidazole, a chlorobenzimidazole, a bromobenzimidazole, a mercaptothiazole, a mercaptobenzthiazole, a mercaptobenzimidazole and a mercap-

tothiadiazole; a triazole, e.g., an aminotriazole, a benzotriazole and a nitrobenzotriazole; a tetrazole, e.g., a mercaptotetrazole, particularly including 1-phenyl-5-mercaptotetrazole and the like; a mercaptopyrimidine; a mercaptotriazine, e.g., a thioketo compound including oxazolinethione; an azaindene, e.g., a triazaindene, a tetraazaindene, particularly including a 4-hydroxy substituted-(1,3,3a,7)tetraazaindene, and a pentaazaindene
 5 benzenethiosulfonic acid, benzenesulfinic acid, benzenesulfonic acid amide, an imidazolium salt, a tetrazolium salt, and a polyhydroxy compound.

In the photographic light-sensitive materials which contain the core/shell type emulsions of the invention, the photographic emulsion layers and the other hydrophilic colloidal layers thereof may contain inorganic or organic hardeners, independently or in combination, which include, for example, a chromium salt such as
 10 chrome alum, chromium acetate and the like; an aldehyde such as formaldehyde, glyoxal, glutaric aldehyde and the like; a N-methylol compound such as dimethylolurea and methyloldimethylhydantoin; a dioxane derivative such as 2,3-dihydroxydioxane; an active vinyl compound such as 1,3,5-triacryloyl-hexahydro-S-triazine, and 1,3-vinylsulfonyl-2-propanol; an active halide such as 2,4-dichloro-6-hydroxy-S-triazine; a mucohalogen acid such as mucochloric acid, and mucophenoxychloric acid.

15 In the photographic light-sensitive materials which contain the core/shell type emulsions of the invention, the photographic emulsion layers and the other hydrophilic colloidal layers thereof may contain the dispersed matters of a water-insoluble or slightly soluble synthetic polymer in order to improve the dimensional stability thereof, for example. Polymers may also be used, independently or in combination, including, for example, alkyl (metha)acrylate, alkoxyalkyl (metha)acrylate, glycidyl (metha)acrylate, (metha)-
 20 acrylamide, a vinyl ester such as vinyl acetate, acrylonitrile, olefin, and styrene; or the polymers each having the monomer-components each comprising a combination of the above-mentioned dispersed matters and acrylic acid, methacrylic acid, α,β -unsaturateddicarboxylic acid, hydroxyalkyl (metha) acrylate, sulfoalkyl (metha)acrylate and styrenesulfonic acid.

The silver halide photographic light-sensitive materials relating to the invention may also contain, if
 25 required, a development accelerator such as benzyl alcohol, a polyoxyethylene compound; an image stabilizer such as a chroman, coumaran, bisphenol or phosphorous acid ester; a lubricant such as a wax; glycerides of a higher fatty acid, the higher alcohol esters of a higher fatty acid and the like; a development regulator; a developing agent; a plasticizer; and a bleaching agent. For the surfactants which may be contained therein, there may also be used a coating aid, a permeability improving agent for a processing
 30 liquid or the like, a defoaming agent or various materials of the anion, cation, non-ion or amphoteric type for controlling various physical properties of the light-sensitive materials. For the antistatic agents, there may effectively be used a diacetyl cellulose, a styrene perfluoroalkylsodium maleate copolymer, an alkali salt of the reaction products of a styrene-maleic anhydride copolymer and p-aminobenzenesulfonic acid. The matting agents include, for example, a polymethacrylic acid methyl, a polystyrene, an alkali-soluble polymer
 35 and the like. In addition, a colloidal silica oxide may also be used. The latexes to be added for improving the physical properties of layers include, for example, a copolymer of an acrylic ester, a vinyl ester or the like and a monomer having the other ethylene group. The gelatin plasticizers include, for example, glycerol and a glycol compound. The thickening agents include, for example, a styrene-sodium maleate copolymer, and an alkylvinylether-maleic acid copolymer.

40 The emulsions each having the silver halide grains of the invention may be provided with a wide latitude, if they are prepared by mixing at least two emulsions which have different average grain size and sensitivity.

The core/shell type silver halide emulsions relating to the invention may effectively be applied to the photographic light-sensitive materials for various applications such as a general black-and-white photog-
 45 raphy, X-ray photography, color photography, infrared photography, microphotography, silver dye bleach photographic process, reversal photography, diffusion transfer photographic process, high contrast photog-raphy, photothermography and heat processable light sensitive materials. Inter alia, they are particularly suitable for a high speed color light-sensitive material.

When applying a core/shell type silver halide emulsion of the invention to a color photographic light-
 50 sensitive material, the silver halide emulsion should be treated in such a process as usually applied to a color light-sensitive material as well as with the materials therefor. In the above-mentioned process, cyan, magenta and yellow couplers are contained in the emulsions each having the aforementioned crystals and having been prepared to be red-, green- and blue-sensitive, respectively. The above-mentioned materials include, for example, the magenta couplers such as 5-pyrazolone, pyrazolobenzimidazole, pyrazolotriazole,
 55 cyanoacetyloumaran, and open-chained acylacetoneitrile; the yellow couplers such as acylacetamide (e.g., a benzoylacetanilide and a pivaloylacetanilide; and the cyan couplers such as naphthol and phenol. The above-mentioned couplers are preferably the non-diffusible ones each having, in the molecules thereof, a hydrophobic group that is the so-called ballast group. The couplers may be of either 4- or 2-equivalent per

silver ion. They may also be colored couplers capable of displaying a color-compensation effect or couplers capable of releasing a development inhibitor while a development is being carried out, (which are called 'non-coloration DIR couplers'). The above-mentioned emulsions may also contain, in addition to the DIR couplers, a non-coloration DIR coupling compound which is capable of producing a colorless coupling reaction products and also releasing a development inhibitor.

According to the invention, the following anti-discoloring agents and color image stabilisers may optionally be used alone or in combination. Such anti-discoloring agents include, for example, a hydroquinone derivative, a gallic acid derivative, a p-alkoxyphenol, a p-oxyphenol derivative, and a bisphenol.

In the light-sensitive materials of the invention, the hydrophilic layers thereof may contain a UV absorbing agent such as a benzotriazole compound substituted by an aryl group, a 4-thiazolidone compound, a benzophenone compound, a cinnamic acid ester compound, a butadiene compound, a benzoxazole compound, or a UV absorptive polymer. It is also possible for such UV absorbing agents to be included in above-mentioned hydrophilic colloidal layers.

In the light-sensitive materials of the invention, the hydrophilic layers thereof may contain a water-soluble dyestuff to serve as a filter dyestuff or for another purpose such as preventing irradiation.

Such dyes as mentioned above include, for example, an oxonol, hemioxonol, styryl, merocyanine, cyanine or azo dye. Among them, the hemioxonol dyes and the merocyanine dyes are particularly useful.

The light-sensitive materials of the invention may contain an anticolor-fogging agent such as a hydroquinone derivative, an aminophenol derivative, a gallic acid derivative or an ascorbic acid derivative.

This invention may also be applied to a multilayered multicolor photographic light-sensitive material comprising a support bearing thereon at least two light-sensitive layers having different spectral sensitivity from each other. Generally, a multilayered color photographic material is provided, on the support thereof, with at least one each of red-, green- and blue-sensitive emulsion layers, respectively. The layers may be arranged in any order, as appropriate. It is usual for the combination to contain cyan forming couplers in a red-sensitive emulsion layer, magenta forming couplers in a green-sensitive emulsion layer and yellow forming couplers in a blue-sensitive emulsion layer, however, a different combination may also be adopted, if necessary.

In the photographic light-sensitive materials of the invention, the photographic emulsion layers and other hydrophilic colloidal layers thereof may be coated on the support or other layers thereof by various well-known coating methods such as a dip-coating method, a roller-coating method, a curtain-coating method or an extrusion-coating method. The preferred methods are described in, for example, U.S. Patent Nos. 2,681,294, 2,761,791 and 3,526,528.

The support of the above-mentioned photographic light-sensitive materials may be, for example, baryta paper, polyethylene-coated paper, synthetic polypropylene paper, glass plate, cellulose acetate film, cellulose nitrate film, polyvinyl acetal film, polypropylene film, polyester film such as polyethyleneterephthalate film or polystyrene film, each of which is ordinarily used and may suitably be selected according to the intended use of the photographic light-sensitive materials.

The above-mentioned supports may also be sublayered, if required.

The photographic light-sensitive materials containing the core/shell type silver halide emulsions relating to the invention may be exposed to light and, after then, developed by any conventional process.

A black-and-white developer is an alkaline solution containing a developing agent such as a hydroxybenzene, an aminophenol or an aminobenzene and, in addition, it may also contain a sulfite, carbonate, bisulfite, bromide or iodide of an alkali metal salt. When the above-mentioned photographic light-sensitive material is for color photographic use, it may be color developed by any convention color developing process. In a reversal process, the development is performed using a black-and-white developer followed by exposure to white-light or a treatment in a bath containing a fogging agent, and further a color-development is made with an alkaline developer containing a color developing agent. There is no particular restriction as to which processes should be used. A typical example of such a process is that, after color-development, a bleach-fixing is made and, if required, followed by washing and a stabilizing process; another example thereof is that, after color-developing, bleaching and fixing are separately performed and, if required, washing and a stabilizing process are further performed. Generally, a color developer comprises an aqueous alkaline solution containing a color developing agent. The color developing agents include, for example, well-known aromatic primary amine developers such as a phenylenediamine, e.g., 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethyl aniline, 4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amin-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -methanesulfonamidoethylaniline and 4-amino-3-methyl-N-ethyl-N- β -methoxyethylaniline.

In addition to the above, it is also possible to use those described in, for example, L.F.A. Mason,

'Photographic Processing Chemistry'. Focal Press, 1966, pp. 226-229; U.S. Patent Nos. 2,193,015 and 2,592,364; and Japanese Patent O.P.I. Publication No. 64933/1973.

The color developers may also additionally contain a pH buffer and/or an antifoggant. They may also further contain, if required, any one of: a water softener, a preserver, an organic solvent, a development accelerator, a dye forming coupler, a competing coupler, a fogging agent, an auxiliary developer, a thickener, a polycarboxylic acid chelating agent, and an oxidation inhibitor.

The photographic emulsion layers are ordinarily bleached after they are color-developed. The bleaching process may be carried out either simultaneously with the fixing process, or independently. The bleaching agents for this purpose include, for example, the compounds of a polyvalent metal such as iron (III), cobalt (IV), chromium (VI) or copper (II) or a peroxy acid, a quinone, or a nitroso compound.

It is possible to add to a bleaching or bleach-fixing liquid, various additives as well as the bleaching accelerators such as those described in, for example, U.S. Patent Nos. 3,042,520 and 3,241,866, Japanese Patent Examined Publication Nos. 8506/1967 and 8836/1967, and the thiol compounds such as those described in, for example, Japanese Patent O.P.I. Publication No. 65732/1978.

Examples

The following examples will further illustrate preferred preparation of the silver halide grains relating to the invention.

Preparation Examples of the silver halide grains

Preparation Example 1

(1-1) Preparation of Inner Core:

By making use of the following six kinds of solutions, a silver iodide emulsion EM-1 was prepared so as to contain silver iodide in an amount of 4 mol% thereof.

(Solution A-1)

Ossein gelatin	39.7 g
Distilled water	3.936 ml
A 10% ethanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	35.4 ml

	Magnesium sulfate	3.6 g
	A 6% solution of nitric acid	75.6 ml
5	Potassium bromide	2.06 g
	(Solution B-1)	
	Ossein gelatin	35.4 g
10	Potassium bromide	807 g
	Potassium iodide	47 g
15	A 10% ethanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	35.4 ml
	Distilled water	1,432 ml
20	(Solution E-1)	
	Silver nitrate	1.200 g
25	A 6% solution of nitric acid	62 ml
	Distilled water	1,467 ml
	(Solution F-1)	
30	A 25% aqueous solution of KBr	An amount required for pAg value adjustment.
	(Solution H-1)	
35	A 6% solution of nitric acid	An amount required for pH value adjustment.
	(Solution I-1)	
40	A 7% aqueous solution of sodium carbonate	An amount required for pH value adjustment.
45	Both Solutions of E-1 and B-1 were added to Solution A-1 in a double-jet precipitation method, at 40° C, by making use of a mixing stirrer described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982. While the double-jet precipitation method was being applied, the pAg and pH value thereof and the rates of addition of both Solutions of E-1 and B-1 were controlled as shown in Table 1. The pAg and pH values were controlled by adjusting the flow rates of both Solutions F-1 and H-1 by making use of a roller-tube pump capable of changing flow rates.	
50	Three minutes after the addition of Solution E-1 was completed, a pH value of the resulted matter was adjusted with Solution I-1.	
	Next, the resultant matter was desalted and washed by a conventional method and dispersed in an aqueous solution containing 125g of ossein gelatin. An aggregate amount of the dispersed matter was then adjusted with distilled water to 4,800ml.	
55	It was observed with an electron microscope that the resulted emulsion was a monodispersed emulsion of 0.09μm in average grain size. Hereinafter, the term, 'grain size', means a length of one side of a cube which is equivalent to a grain in volume.	

Table 1

Time (min)	Rate of adding solution (ml/min)		pAg	pH
	Solution E-1	Solution B-1		
0.00	15.9	15.9	9.0	2.0
1.50	15.9	15.9	9.0	2.0
2.00	15.9	15.2	9.0	2.0
5.00	15.9	15.2	9.0	2.0
10.30	29.1	28.4	9.0	2.0
13.72	39.8	39.1	9.0	2.0
16.37	49.2	48.5	9.0	2.0
17.95	55.0	54.3	9.0	2.0
18.65	57.8	57.1	9.0	2.0
20.55	65.7	65.0	9.0	2.0
22.25	73.2	72.5	9.0	2.0
25.20	87.2	86.3	9.0	2.0
26.50	93.8	92.9	9.0	2.0
27.70	100.2	99.9	9.0	2.0
28.85	106.3	105.3	9.0	2.0
29.95	112.3	111.1	9.0	2.0
30.95	118.1	117.0	9.0	2.0
31.92	123.8	122.6	9.0	2.0
32.10	124.8	123.5	9.0	2.0

(1-2) Provision of the 5th Shell:

Emulsion EM-2 was prepared, by using the following 5 kinds of solution, in such a process that the above-mentioned Emulsion EM-1 was used as a seed emulsion to which silver iodobromide shells each having a silver iodide content of 2 mol% were provided.

(Solution A-2)

	Oss in g latin	34.54 g
5	Distilled water	8.642 ml
	A 10% ethanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	20 ml
10	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	181.32 mg
	A 28% aqueous ammonia	117.4 ml
15	A 56% aqueous solution of acetic acid	154 ml
	Magnesium sulfate	16 g
20	Seed emulsion (EM-1)	An equivalent amount to 0.329 mol

(Solution B-2)

25	Ossein gelatin	18.72 g
	KBr	763.8 g
30	KI	21.8 g
	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	2.17 g
35	Magnesium sulfate	7.4 g
	Distilled water	1,578 ml

(Solution E-2)

40	AgNO ₃	1,142.4 g
	A 28% aqueous ammonia	931.4 ml
45	Add distilled water to make	1,921 ml

(Solution F-2)

50	A 50% aqueous solution of KBr	An amount required for pAg value adjustment.
----	-------------------------------	--

(Solution G-2)

55	A 56% aqueous solution of acetic acid	An amount required for pH value adjustment.
----	---------------------------------------	---

Both Solutions of E-2 and B-2 were added to Solution A-2 in a double-jet precipitation method, at 40° C, by making use of a mixing stirrer described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982, by taking a time for 32.5 minutes at a minimum so as not to produce any small grains during the addition thereof. While the double-jet precipitation method was being applied, the pAg and pH value thereof and the adding rates of both Solutions of E-2 and B-2 were controlled as shown in Table 2. The pAg and pH values were controlled by adjusting the flow rates of Solutions F-2, G-2 and B-2 by making use of a roller-tube pump capable of changing flow rates.

After the addition of Solution E-2 was completed, the pAg value was adjusted to 10.4 with Solution G-2 and, two minutes after then, the pH value was adjusted to 6.0 with Solution F-2, respectively.

Table 2

Time (min)	Rate of adding solution (ml/min)		pAg	pH
	Solution E-2	Solution B-2		
0.00	16.24	15.44	8.50	8.00
5.43	41.87	40.15	8.54	7.95
8.17	60.36	58.69	8.58	7.88
10.38	76.58	74.98	8.64	7.78
13.62	83.78	82.24	8.71	7.66
16.33	81.82	80.33	8.78	7.53
19.07	75.04	73.56	8.84	7.42
21.78	66.98	65.53	8.90	7.31
24.51	59.36	57.93	8.95	7.22
26.83	53.65	51.93	8.99	7.15
29.97	49.56	47.82	9.00	7.06
32.48	46.47	44.71	9.00	7.00

Next, the resultant matter was desalted and washed by a conventional process, and was dispersed in an aqueous solution containing 128.6g of ossein gelatin. An aggregate amount thereof was then adjusted to 3,000ml with distilled water.

It was observed with an electron microscope that the resulted emulsion was an excellent monodispersed emulsion of 0.27 μ m in average grain size and of 12% in the variation coefficient of grain size distribution.

(1-3) Provision of the 4th Shell:

Emulsion EM-3 was prepared, by using the following 5 kinds of solution, in such a process that the above-mentioned Emulsion EM-2 was used as a seed emulsion to which silver iodobromide shells each having a silver iodide content of 2.6 mol% were provided.

(Solution A-3)

Ossein gelatin	34.0 g
Distilled water	7.779 ml
A 10% ethanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	20 ml
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	405 mg
A 28% aqueous ammonia	117.3 ml
A 56% aqueous solution of acetic acid	72 ml
Seed emulsion (EM-2)	An equivalent amount to 0.303 mol

(Solution B-3)

Ossein gelatin	18.74 g
KBr	760.2 g
KI	28.4 g
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	1.35 g
Distilled water	1,574 ml

(Solution E-3)

AgNO ₃	1.148 g
A 28% aqueous ammonia	937 ml

Add distilled water to make 1,930 ml

(Solution F-3)

A 50% aqueous solution of KBr An amount required for pH value adjustment.

(Solution G-3)

A 56% aqueous solution of acetic acid An amount required for pH value adjustment.

Both Solutions of E-3 and B-3 were added to Solution A-3 in a double-jet precipitation method, at 40° C, by making use of a mixing stirrer described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982, by taking a time for 56.5 minutes at a minimum so as not to produce any small grains during

the addition thereof. During the double-jet precipitation method, the pAg and pH values and the rates of addition of both Solutions of E-3 and B-3 were controlled as shown in Table 3. The pAg and pH values were controlled by adjusting the flow rates of Solutions F-3, G-3 and B-3 by making use of a roller-tube pump capable of changing flow rates.

Two minutes after the addition of Solution E-3 was completed, the pAg value was adjusted to 10.4 with Solution G-3 and, two minutes after then, the pH value was adjusted to 6.0 with Solution F-3, respectively.

Next, the resultant matter was desalted and washed by a conventional process, and was dispersed in an aqueous solution containing 128.1g of ossein gelatin. After then, an aggregate amount thereof was adjusted to 3,000ml with distilled water.

It was observed with an electron microscope that the resulted emulsion was an excellent monodispersed emulsion of 0.80 μ m in average grain size and of 10% in the variation coefficient of grain size distribution.

Table 3

Time (min)	Rate of adding solution (ml/min)		pAg	pH
	Solution E-3	Solution B-3		
0.00	5.77	5.49	9.0	9.00
9.43	10.29	9.79	9.0	8.96
14.17	13.91	13.24	9.0	8.93
18.88	18.96	18.04	9.0	8.88
23.62	23.91	24.65	9.0	8.83
28.33	35.09	33.81	9.0	8.76
33.05	44.20	42.92	9.0	8.66
37.78	53.27	52.01	9.0	8.54
42.50	55.56	54.31	9.0	8.40
47.23	56.37	55.12	9.0	8.27
51.95	58.00	56.75	9.0	8.13
56.53	56.01	54.76	9.0	8.00

(1-4) Provision of Highly iodide-containing Shell, Intermediate Shell and the Outermost Shell of the Invention:

Emulsion EM-4 was prepared, by using the following 7 kinds of solutions, in such a process that the above-mentioned Emulsion EM-3 was used as a seed emulsion to which a highly iodide-containing shell, an intermediate shell and the outermost shell were provided.

(Solution A-4)

	Ossein gelatin	22.5 g
5	Distilled water	6,884 ml
	A 10% ethanol solution of sodium polyisopropylene-polyethyleneoxy-disuccinate	20 ml
10	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	Amount shown in Table-4
	A 28% aqueous ammonia	469 ml
15	A 56% aqueous solution of acetic acid	258 ml
	Seed emulsion (EM-3)	An equivalent amount to 0.8828 mol
20		

(Solution B-4)

	Ossein gelatin	24 g
25	KBr	Amount shown in Table-5
	KI	Amount shown in Table-5
30	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	Amount shown in Table-5
	Distilled water	1,978 ml

(Solution C-4)

	Ossein gelatin	24 g
	KBr	Amount shown in Table-6
40	KI	Amount shown in Table-6

	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	Amount shown in Table-6
5	Distilled water	1,978 ml
	(Solution D-4)	
	Ossein gelatin	40 g
10	KBr	Amount shown in Table-7
	KI	Amount shown in Table-7
15	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	Amount shown in Table-7
	Distilled water	3,296 ml
20	(Solution E-4)	
	AgNO ₃	1,109 g
	A 28% aqueous ammonia	904 ml
25	Add distilled water to make	1,866 ml
	(Solution F-4)	
30	A 50% aqueous solution of KBr	An amount required for pAg value adjustment
	(Solution G-4)	
35	A 56% aqueous solution of acetic acid	An amount required for pH value adjustment

Both Solutions of E-4 and B-4 were added to Solution A-4 in a double-jet precipitation method, at 50 °C, by making use of a mixing stirrer described in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982, by taking a time for 46.6 minutes. At the same time when the addition of Solution B-4, Solution C-4 was added thereto. After 35.9 minutes, i.e. when the addition of Solution C-4 was completed, Solution D-4 was added thereto and after 25.5 minutes, the addition of Solution D-4 was completed. During the double-jet precipitation method, the pAg and pH values and the rates of addition of the solutions of E-4, B-4, C-4 and D-4 were controlled as shown in Table-8. The pAg and pH values were controlled by adjusting the flow rates of Solutions F-4 and G-4 by making use of a roller-tube pump capable of changing flow rates.

Two minutes after the addition of Solution E-4 was completed, the pAg value thereof was adjusted to 10.4 by, Solution F-4 and, after two minutes, the pH value thereof was further adjusted to 6.0 by Solution G-4, respectively.

Next, the resultant matter was desalted and washed by a conventional method and was dispersed in an aqueous solution containing 127g of ossein gelatin. After then, the resulted dispersed matter was adjusted to an aggregate amount of 3,000ml with distilled water.

It was observed with a electron microscope that the resultant emulsion was an excellent monodispersed emulsion of 1.60μm in average grain size and of 11% in the variation coefficient of grain size distribution.

The emulsion EM-4 is a core/shell type silver iodobromide emulsion having the silver iodide contents of 15 mol%, 5 mol% and 0.3 mol% in the order arranged from the inside of each grain. (i.e., $I_1 = 0.3$, $I_2 = 0.5$ and $I_3 = 5$, respectively)

Tabl 4

Content of Solution A-4 .

Emulsion No.	4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (mg)
EM-4	646
EM-5	646
EM-6	646
EM-7	646
EM-8	646
EM-9	646
EM-10	646
EM-11	646
EM-12	646
EM-13	646
EM-14	646
EM-15	646
EM-16	646
EM-17	646
EM-18	646
EM-19	646
EM-20	646
EM-21	646
EM-22	646
EM-23	646
EM-24	646

Emulsion No.	4-hydroxy-6-methyl-1,3,3a,7-tetraazaindole (mg)
EM-25	646
EM-26	646
EM-27	646
EM-28	323
EM-29	323
EM-30	323
EM-31	323
EM-32	646
EM-33	646
EM-34	646
EM-35	646
EM-36	646
EM-37	646
EM-38	646
EM-39	646

Tabl 5
Content of Solution B-4

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zaindene (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ mol%
EM-4	2560	848	209	15
EM-5	2560	848	209	15
EM-6	2560	848	209	15
EM-7	2560	848	209	15
EM-8	2560	848	209	15
EM-9	2560	848	209	15
EM-10	2560	948	69.7	3
EM-11	2560	918	111	8
EM-12	2560	898	139	10
EM-13	2560	798	278	20
EM-14	2560	698	418	30
EM-15	2560	598	557	40
EM-16	2560	598	557	40
EM-17	2560	498	697	50
EM-18	2560	498	697	50
EM-19	2560	848	209	15
EM-20	2560	848	209	15
EM-21	2560	848	209	15
EM-22	2560	848	209	15
EM-23	2560	848	209	15

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zaindene (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ m 1%
EM-24	2560	848	209	15
EM-25	2560	848	209	15
EM-26	2560	748	348	25
EM-27	2560	848	209	15
EM-28	1280	848	209	15
EM-29	1280	848	209	15
EM-30	1280	848	209	15
EM-31	1280	848	209	15
EM-32	2560	848	209	15
EM-33	2560	848	209	15
EM-34	2560	848	209	15
EM-35	2560	748	348	25
EM-36	2560	648	488	35
EM-37	2560	648	488	35
EM-38	2560	918	111	8
EM-39	2560	918	111	8

Tabl 6
Content of Solution C-4

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zaindene (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ mol%
EM-4	2560	948	69.7	5
EM-5	2560	848	209	15
EM-6	2560	868	181	13
EM-7	2560	898	139	10
EM-8	2560	978	27.9	2
EM-9	2560	996	4.18	0.3
EM-10	2560	948	69.7	5
EM-11	2560	948	69.7	5
EM-12	2560	948	69.7	5
EM-13	2560	948	69.7	5
EM-14	2560	948	69.7	5
EM-15	2560	948	69.7	5
EM-16	2560	996	4.18	0.3
EM-17	2560	948	69.7	5
EM-18	2560	996	4.18	0.3
EM-19	2560	948	69.7	5
EM-20	2560	948	69.7	5
EM-21	2560	948	69.7	5
EM-22	2560	948	69.7	5
EM-23	2560	898	139	10

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zaind ne (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ mol%
EM-24	2560	898	139	10
EM-25	2560	898	139	10
EM-26	2560	828	237	17
EM-27	2560	948	69.7	5
EM-28	1280	948	69.7	5
EM-29	1280	996	4.18	0.3
EM-30	1280	948	69.7	5
EM-31	1280	996	4.18	0.3
EM-32	2560	948	69.7	5
EM-33	2560	948	69.7	5
EM-34	2560	948	69.7	5
EM-35	2560	898	139	10
EM-36	2560	898	139	10
EM-37	2560	924	104	7.5
EM-38	2560	956	55.7	4
EM-39	2560	996	4.18	0.3

Table 7

Content of Solution D-4

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zaindene (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ mol%
EM-4	4268	1660	6.97	0.3
EM-5	4268	1660	6.97	0.3
EM-6	4268	1660	6.97	0.3
EM-7	4268	1660	6.97	0.3
EM-8	4268	1660	6.97	0.3
EM-9	4268	1660	6.97	0.3
EM-10	4268	1660	6.97	0.3
EM-11	4268	1660	6.97	0.3
EM-12	4268	1660	6.97	0.3
EM-13	4268	1660	6.97	0.3
EM-14	4268	1660	6.97	0.3
EM-15	4268	1660	6.97	0.3
EM-16	4268	1660	6.97	0.3
EM-17	4268	1660	6.97	0.3
EM-18	4268	1660	6.97	0.3
EM-19	4268	1660	0	0
EM-20	4268	1657	11.6	0.5
EM-21	4268	1641	34.8	1.5
EM-22	4268	1591	104	4.5
EM-23	4268	1641	34.8	1.5

Emulsion No.	4-hydroxy-6-methyl- -1,3,3a,7-tetra- zainden (mg)	KBr (g)	KI (g)	$\frac{KI}{(KBr+KI)}$ mol%
EM-24	4268	1591	104	4.5
EM-25	4268	1532	185	8
EM-26	4268	1482	255	11
EM-27	4268	1660	6.97	0.3
EM-28	2134	1660	6.97	0.3
EM-29	2134	1660	6.97	0.3
EM-30	2134	1660	6.97	0.3
EM-31	2134	1660	6.97	0.3
EM-32	4268	1660	6.97	0.3
EM-33	4268	1660	6.97	0.3
EM-34	4268	1660	6.97	0.3
EM-35	4268	1581	115	5
EM-36	4268	1581	115	5
EM-37	4268	1581	115	5
EM-38	4268	1660	6.97	0.3
EM-39	4268	1660	6.97	0.3

Table 8

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	B-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	8.70	9.00
18.00	8.89	8.80	-	-	8.70	9.00
27.00	9.75	9.65	-	-	8.70	9.00
36.00	10.55	10.45	-	-	8.70	9.00
45.00	11.29	11.18	-	-	8.70	9.00
46.60	11.51	11.40	11.40	-	8.70	9.00
54.80	16.44	-	18.12	-	8.93	8.86
63.05	21.38	-	24.73	-	9.30	8.66
72.05	32.84	-	60.87	-	9.96	8.31
75.50	26.31	-	54.69	-	10.19	8.21
82.50	24.12	-	23.88	23.88	10.20	8.04
90.06	21.89	-	-	21.67	10.20	7.86
99.08	20.13	-	-	19.93	10.20	7.66
108.00	19.25	-	-	19.06	10.20	7.50

Preparation Example 2

The emulsions, EM-5, EM-6, EM-7, EM-8 and EM-9, were prepared in the same manner as in (1-4) of the above-mentioned preparation example, except that they employed the 7 kinds of solutions described in (1-4) of the preparation example and added KBr, KI and 4-hydroxy-6-methyl-1,3,3a,7-tetraindene in the amounts designated in Tables 4, 5, 6 and 7, respectively.

The resultant emulsions were monodispersed emulsions each of 1.60 μ m in average grain size and their variation coefficients of grain size distribution were 17%, 15%, 12%, 16% and 16%, respectively.

Preparation Example 3

The emulsions, EM-10 through EM-26, were prepared in the same manner as in (1-4) of the Preparation Example 1, except that the 7 kinds of solutions designated in the Preparation Example 1 and, KBr, KI and 4-hydroxy-6-methyl-1,3,3a,7-tetraindene were used in the amounts designated in Tables 4, 5, 6 and 7, respectively.

These emulsions were monodispersed, having an average grain size of 1.60 μ m and the variation coefficients of the grain size distributions of 10%, 10%, 11%, 12%, 13%, 18%, 19%, 35%, 39%, 10%, 11%, 11%, 12%, 12%, 12% and 13%, respectively.

Preparation Example 4

The emulsions, EM-28 and EM-29, were prepared in the same manner as in (1-4) of the Preparation

Example 1, except that the 7 kinds of solutions designated in the Preparation Example 1 and, KBr, KI, and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were used in the amounts designated in Tables 4, 5, 6 and 7, respectively.

Further, the Emulsion EM-27 was prepared in such a manner that the pAg and pH values and rates of addition thereof were changed to those designated in Table-9 in the course of the mixation thereof; and the Emulsion EM-30 and 31 were also prepared as shown in Table-10.

The above-mentioned emulsions were monodispersed, having the average grain size of 1.6 μ m and the variation coefficients of the grain size distributions of 9%, 18%, 19%, 32% and 34%, respectively.

Table 9

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	E-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	8.70	9.00
18.00	8.89	8.80	-	-	8.70	9.00
27.00	9.75	9.65	-	-	8.70	9.00
36.00	10.55	10.45	-	-	8.70	9.00
45.00	11.29	11.18	-	-	8.70	9.00
46.60	11.51	11.40	11.40	-	8.70	9.00
54.80	16.44	-	18.12	-	8.93	8.86
63.05	21.38	-	24.73	-	9.30	8.66
72.05	32.84	-	60.87	-	9.96	8.31
75.50	26.31	-	54.69	-	10.00	8.21
82.50	24.12	-	23.88	23.88	10.00	8.04
90.06	21.89	-	-	21.67	10.00	7.86
99.08	20.13	-	-	19.93	10.00	7.66
108.00	19.25	-	-	19.06	10.00	7.50

Table 10

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	E-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	10.20	9.00
18.00	8.89	8.80	-	-	10.20	9.00
27.00	9.75	9.65	-	-	10.20	9.00
36.00	10.55	10.45	-	-	10.20	9.00
45.00	11.29	11.18	-	-	10.20	9.00
46.60	11.51	11.40	11.40	-	10.20	9.00
54.80	16.44	-	18.12	-	10.20	8.86
63.05	21.38	-	24.73	-	10.20	8.66
72.05	32.84	-	60.87	-	10.20	8.31
75.50	26.31	-	54.69	-	10.20	8.21
82.50	24.12	-	23.88	23.88	10.20	8.04
90.06	21.89	-	-	21.67	10.20	7.86
99.08	20.13	-	-	19.93	10.20	7.66
108.00	19.25	-	-	19.06	10.20	7.50

Preparation Example 5

The emulsion EM-32 was prepared in the same manner as in (1-4) of the Preparation Example 1, except that the 7 kinds of solutions designed in the Preparation Example 1 and, KBr, KI and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene were used in the amounts designated in Tables 4, 5, 6 and 7, respectively, and the pAg and pH values and rates of addition of E-4, B-4, C-4 and D-4 thereof were further changed to those designated in Table-11 during mixing; and the Emulsion EM-33 was prepared as shown in Table-12, and Emulsion EM-34 was further prepared as shown in Table-13, respectively. The above-mentioned emulsions were the monodispersed having the average grain size of 1.6 μ m and the variation coefficients of the grain size distributions of 10%, 10% and 12%, respectively.

Table 11

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	E-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	8.70	9.00
18.00	8.89	8.80	-	-	8.70	9.00
27.00	9.75	9.65	-	-	8.70	9.00
28.50	9.89	9.80	9.80	-	8.70	9.00
36.00	10.55	-	10.45	-	8.70	9.00
45.00	11.29	-	11.18	-	8.70	9.00
46.60	11.51	-	11.40	-	8.70	9.00
54.80	16.44	-	18.12	-	8.93	8.86
63.05	21.38	-	24.73	-	9.30	8.66
72.05	32.84	-	60.87	-	9.96	8.31
75.50	26.31	-	54.69	-	10.19	8.21
82.50	24.12	-	23.88	23.88	10.20	8.04
90.06	21.89	-	-	21.67	10.20	7.86
99.08	20.13	-	-	19.93	10.20	7.66
108.00	19.25	-	-	19.06	10.20	7.50

Table 12

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	E-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	8.70	9.00
13.90	8.47	8.39	8.39	-	8.70	9.00
18.00	9.75	-	9.63	-	8.70	9.00
27.00	9.89	-	9.80	-	8.70	9.00
36.00	10.55	-	10.45	-	8.70	9.00
45.00	11.29	-	11.18	-	8.70	9.00
46.60	11.51	-	11.40	-	8.70	9.00
54.80	16.44	-	18.12	-	8.93	8.86
63.05	21.38	-	24.73	-	9.30	8.66
72.05	32.84	-	60.87	-	9.96	8.31
75.50	26.31	-	54.69	-	10.19	8.21
82.50	24.12	-	23.88	23.88	10.20	8.04
90.06	21.89	-	-	21.67	10.20	7.86
99.08	20.13	-	-	19.93	10.20	7.66
108.00	19.25	-	-	19.06	10.20	7.50

Table 13

Time (min)	Rate of adding solution (ml/min)				pAg	pH
	E-4	B-4	C-4	D-4		
0.00	7.07	7.00	-	-	8.70	9.00
18.00	8.89	8.80	-	-	8.70	9.00
27.00	9.75	9.65	-	-	8.70	9.00
36.00	10.55	10.45	-	-	8.70	9.00
45.00	11.29	11.18	-	-	8.70	9.00
46.60	11.51	11.40	-	-	8.70	9.00
54.80	16.44	18.12	-	-	8.93	8.86
63.05	21.38	24.73	-	-	9.30	8.66
68.85	28.76	48.02	48.02	-	9.72	8.43
72.05	32.84	-	60.87	-	9.96	8.31
75.50	26.31	-	54.69	-	10.19	8.21
82.50	24.12	-	23.88	23.88	10.20	8.04
90.06	21.89	-	-	21.67	10.20	7.86
99.08	20.13	-	-	19.93	10.20	7.66
108.00	19.25	-	-	19.06	10.20	7.50

Preparation Example 6

The emulsions EM-35, EM-36 and EM-37 were prepared in the same manner as in (1-4) of the Preparation Example 1, except that the 7 kinds of solutions designated in the Preparation Example 1 and, KBr, KI and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene were used in the amounts designated in Tables 4, 5, 6 and 7, respectively.

Further, the Emulsions EM-38 and EM-39 were prepared in such a manner that the pAg and pH values and the rates of addition of E-4, B-4, C-4 and D-4 thereof were changed to those designated in Table 12 during mixing.

The above-prepared emulsions were monodispersed having an average grain size of 1.6 μ m and variation coefficients of the grain size distributions of 12%, 14%, 13%, 9% and 11%, respectively.

E. Examples of the preparation of the photographic light-sensitive materials:

The examples of the invention will now be described in detail.

<Example 1>

The effects of an intermediate shell are shown by making use of the above-mentioned Emulsions EM-5, EM-6, EM-7, EM-4, EM-8 and EM-9.

Each effect thereof on sensitivity, fog, graininess, exposure range, sharpness and interlayer sensitivity was examined.

The effects thereof on the sensitivity, fog, graininess, exposure range and sharpness were measured with monolayered samples prepared for this purpose.

The effects on the multilayer sensitivity were examined with a multilayer red color light-sensitive material having three light-sensitive layers, a blue light-sensitive layer, a green light-sensitive layer and a red light-sensitive layer.

The processes for preparing the samples and the methods of measuring the characteristics of the samples were as follows:

Preparation of a single-color sensitive coating sample (called a monolayered sample):

The following details relate to a material of the invention, comprising a light-sensitive material having two layers, one is an emulsion-coated layer containing a coupler and the other is a protective layer.

In this example, a magenta-color forming coupler was used. Namely, 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)benzamido]-5-pyrazolone was used in this example to serve as the magenta color forming coupler.

Tricresyl phosphate (TCP) was used as the high boiling solvent for dissolving the couplers.

The couplers were oil-protect-dispersed by a conventional method.

The silver iodobromide emulsions (EM-4 through EM-9) described in the aforementioned preparation examples were chemically sensitized by conventional method and were additionally green-color-sensitized with a green-color-sensitive spectral sensitizer.

Each of the layers of this example was prepared in the following manner:

1st layer ...

A high-speed green-sensitive emulsion layer containing 1.9g of the above-described silver iodobromide emulsions which were chemically sensitized and color-sensitized, and a dispersed matter comprising 1.9g of gelatin and 0.06g of DNP (which stands for ditertiary nonyl phenol) dissolving 0.20g of the magenta coupler and 0.04g of a colored magenta coupler.

2nd layer ...

A yellow-filter layer containing 0.15g of yellow colloidal silver, 0.11g of DBP (which stands for dibutyl-terephthalate) dispersed matter in which 0.2g of an anti-contaminating agent was dissolved and 1.5g of gelatin;

Each of the above-mentioned two layers was added with a gelatin hardener and a surface active agent, as well as the above-mentioned compositions.

For measuring the sensitometric characteristics and the graininess, each of the samples was exposed to light through a wedge in an ordinary method; and for measuring the graininess, each of the samples was exposed to light through a square wave frequency wedge; and each of them was processed in the following steps:

40	Color-developing	3 min. 15 s
	Bleaching	6 min. 30 s
45	Washing	3 min. 15 s
	Fixing	6 min. 30 s
50	Washing	3 min. 15 s
	Stabilizing	1 min. 30 s
55	Drying	

The composition of the processing liquids used in the above-mentioned processing steps are shown below:

[Color developer]

5	4-amino-3-methyl-N-(β -hydroxyethyl)- aniline.sulfate	4.57 g
	Sodium sulfite, anhydrated	4.25 g
	Hydroxylamine 1/2 sulfate	2.0 g
10	Potassium carbonate, anhydrated	37.5 g
	Sodium bromide	1.3 g
15	Trisodium nitrilotriacetate, monohydrated	2.5 g
	Potassium hydroxide	1.0 g
20	Add water to make	1 liter

[Bleaching liquid]

25	Iron ammonium ethylene- diaminetetraacetate	100.0 g
	Diammonium ethylenediaminetetraacetate	10.0 g
30	Ammonium bromide	150.0 g
	Glacial acetic acid	10.0 ml
35	Add water to make	1 liter
	Adjust the pH value with aqueous ammonia to pH 6.0	

[Fixing liquid]

40	Ammonium thiosulfate	175.0 g
	Ammonium sulfite, anhydrated	8.6 g
45	Sodium metasilfite	2.3 g
	Add water to make	1 liter
	Adjust the pH value with acetic acid to pH 6.0	

[Stabilizing liquid]

50	Formalin (a 37% aqueous solution)	1.5 ml
55	Konidax (mfd. by Konishiroku Photo Ind. Co., Ltd., Japan.)	7.5 ml
	Add water to make	1 liter

With respect to the developed samples, the respective sensitometric characteristics, graininess and sharpness thereof were measured by making use of green-light.

Fogginess ...

5

A so-called minimum optical density on a characteristic curve, obtained from a sensitometry. (The higher a value of such a minimum optical density is, the more a fogginess is. Therefore, a high minimum optical density is not preferred.)

10 Sensitivity ...

The reciprocal of a quantity of exposure (in antilog) which gives an optical density of fog +0.1 on a characteristic curve. (In the table showing the results of the example, the reciprocal numbers each are expressed as a value relative to the sensitivity of the comparative example which is regarded as the value 100.: The higher the value of such a reciprocal number, the better the sensitivity. Therefore, a high reciprocal number is preferred.)

Sharpness ...

20 The improvement effects on the sharpness of an image were detected by obtaining a MTF (which stands for Modulation Transfer Function) so as to compare the samples with each other with respect to the MTFs obtained when each spatial frequency is 10 lines per mm. The greater the MTF value, the better the sharpness. That is preferred.

25 Graininess ...

The standard deviation of a density value variation is obtained when scanning a dye image having a ratio of a RMS to a dye image density of $D_{min} + 0.8$ with a micro-densitometer having a round scanning aperture of 25 μm , and 1.000 times this value is expressed as a value relative to the standard deviation value of a controlled sample regarded as a value of 100. The higher the value, the coarser the graininess. That is not preferred.

Exposure range ...

35 The greater the difference between an exposure quantity (at a logarithmic value) giving an optical density with a fog of +0.1 and an exposure quantity (at a logarithmic value) giving a maximum optical density of -0.1 is, the wider an exposure range is. It is, therefore, preferred that a difference therebetween is greater.

Preparation of a multilayered color photographic material (hereinafter called a multilayered sample):

40 The silver iodobromide emulsions (EM-4 through EM-9) described in the above-mentioned preparation examples were chemically sensitized by conventional methods so as to prepare a color photographic material comprising 9 layers including 3 kinds of light-sensitive layers, a blue light-sensitive layer, a green light-sensitive layer and a red light-sensitive layer, in the following manner. The emulsions EM-4 to EM-9 each chemically sensitized were changed only in a green-sensitive high speed layer that was the 5th layer.

45 In each sample, the same and common emulsions were used in the other light-sensitive layers than the 5th layer.

The sample was prepared by coating the aforementioned layers, in sequence, on a transparent support which comprises a sub-layered cellulose triacetate film and bears thereon an antihalation layer (containing 0.40g of black colloidal silver and 3.0g of gelatin). In all the examples mentioned below, the amounts of every material to be added to the light-sensitive materials is indicated in an amount per square meter, and both the silver halide emulsion and colloidal silver are indicated in terms of silver content.

1st layer ...

55 A low speed red-sensitive emulsion layer (hereinafter called an RL layer) containing 1.4g of a low speed red-sensitive silver iodobromide emulsion layer (containing silver iodide of 7 mol%) which was color-sensitized to red; 1.2g of gelatin; 0.65g of tricresyl phosphate (TCP) in which 0.8g of 1-hydroxy-4(β -methoxyethylaminocarbonylmethoxy)-N-[β -(2,4-di-*t*-amylphenoxy)butyl]-2-naphthamid [hereinafter called C-

1]; 0.075g of 1-hydroxy-4-[4-(1-hydroxy- δ -acetamido-3,6-disulfo-2-naphthylazo)phenoxy]-N-[δ -(2,4-di-t-amylphenoxy)-butyl-2-naphthamido]disodium [hereinafter called a colored cyan coupler (CC-1)]; and 0.015g of 1-hydroxy-2[δ -2,4-di-t-amylphenoxy)n-butyl]naphthamide and 0.07g of 4-octadecyl succinimido-2-(1-phenyl-5-tetrazolylthio)-1-indanone were dissolved [hereinafter called a DIR compound (D-1)] were dissolved.

5

2nd layer ...

A high speed red-sensitive emulsion layer (hereinafter called an RH layer) containing 1.3g of a high speed red-sensitive silver iodobromide emulsion; 1.2g of gelatin; and 0.23g of TCP in which 0.21g of cyan coupler (C-1); and 0.02g of colored cyan coupler (CC-1) were dissolved.

10

3rd layer ...

An intermediate layer (hereinafter called an IL layer) containing 0.04g of dibutyl phthalate (hereinafter called DBP) in which 0.07g of 2,5-di-t-octylhydroquinone [hereinafter called an antistaining agent (HQ-1)] were dissolved; and 0.8g of gelatin.

15

4th layer ...

A low speed green-sensitive emulsion layer (hereinafter called a GL layer) containing 0.80g of a low speed silver iodobromide emulsion (containing silver iodide of 6 mol%) which was green-sensitized; 2.2g of gelatin; 0.95g of TCP in which 0.8g of 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-amylphenoxyacetamido)-5-pyrazolone [hereinafter called a magenta coupler (M-1)]; 0.15g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccineimidoanilino)-5-pyrazolone [herein after called a colored magenta coupler (CM-1)]; and 0.016g of the DIR compound (D-1) were dissolved.

20

5th layer ...

A high speed green-sensitive emulsion layer (hereinafter called a GH layer) containing 1.8g of a high speed green-sensitive silver iodobromide emulsion which was green-sensitized; 1.9g of gelatin; 0.25g of TCP in which 0.20g of the magenta coupler (M-1); and 0.049g of the colored magenta coupler (CM-1) were dissolved.

30

6th layer ...

35

A yellow filter layer (hereinafter called a YC layer) containing 0.15g of yellow colloidal silver; 0.11g of DBP in which 0.2g of the antistaining agent (HQ-1) was dissolved; and 1.5g of gelatin.

7th layer ...

40

A low speed blue-sensitive emulsion layer (hereinafter called a BL layer) containing a low speed silver iodobromide emulsion (containing silver iodide of 4 mol%) which was blue-sensitized; 1.9g of gelatin; and 0.6g of TCP in which 1.5g of α -pivaloyl- α -(1-benzyl-2-phenyl-3,5-dioximidazolidine-4-yl)-2'-chloro-'-[α -dodecyloxycarbonyl]ethoxycarbonyl]acetanilide [hereinafter called Y-1] was dissolved.

45

8th layer ...

A high speed blue-sensitive emulsion layer (hereinafter called a BH layer) containing 1.0g of a high speed silver iodobromide emulsion which was color-sensitized to blue; 1.5g of gelatin; and 0.65g of TCP in which 1.30g of yellow coupler (Y-1) were dissolved.

50

9th layer ...

A protective layer (hereinafter called a PR layer) containing 2.3g of gelatin.

55

Measurement of multilayer Sensitivity:

The prepared multilayered color photographic material was exposed to white light through a wedge and

processed in the above-mentioned processing steps. A green optical sensitivity was obtained therefrom by a sensitometry. (The definition of sensitivity is the same as that in the case of the above-mentioned single layer coated sample.)

5 Results of Example 1 (The effects of the intermediate shell):

Table-14 shows the results of the fog, sensitivity, graininess, exposure range and sharpness of the single-color-sensitive coated sample as well as the results of the multilayered sample.

The core/shell type emulsions (EM-4 and EM-7) each provided with a highly iodide-containing shell, an intermediate shell and the outermost shell in accordance with the invention are capable of displaying remarkably higher sensitivity, as compared with such conventional core/shell type emulsions as EM-5 and EM-9 neither of which were provided with any intermediate shell interposed between the outermost shell that is a low iodide-containing shell and a highly iodide-containing shell so as to contain iodide in an intermediate amount; such a core/shell type emulsion as EM-6 provided with an intermediate shell but having no reasonable difference in iodide contents between a highly iodide-containing shell and the intermediate shell; and such a core/shell type emulsion as EM-8 having no reasonable difference in iodide contents between the outermost shell and an intermediate shell.

It is also found that the above-mentioned results are particularly remarkable with regard to multilayer sensitivity and that the core/shell type emulsions of the invention are more effective in a multi-layered color light-sensitive material.

Other core/shell type emulsions outside the scope of the invention tend to broaden the grain size distribution and increase fogs, so bearing this in mind, it may be preferred not to use them.

<Example 2>

Table-15 shows the effects of varying the iodide content in highly iodide-containing shells, prepared using the emulsions EM-4, EM-5 and EM-9 to EM-18 of the above-mentioned Preparation Example and in the same manner as in Example 1.

The emulsions EM-10 to EM-15 are examples in which the intermediate shells and the outermost shells each have constant iodide content while the iodide content of the highly iodide-containing shells was varied. It is found therefrom that the higher the iodide content in a highly iodide-containing shell, the better the sensitivity.

An emulsion having an iodide content of 40 or 50 mol% in the highly iodide-containing shell thereof as EM-15 or EM-17 tends to show a reduced sensitizing effect. This is supposedly due to the fact that the grain size distribution was broadened, and it is found that the emulsions of the invention may be able to enjoy a satisfactory sensitization effect as compared with any emulsions each having the same highly iodide-containing shell, such as EM-16 and EM-18, which are other than those of the invention.

<Example 3>

Table-16 shows, similarly to the above, the effects of the iodide contents in the low iodide-containing shells and the intermediate shells.

The lower the iodide content in the outermost shell, the greater the sensitizing effects of the invention.

Particularly in multilayer sensitivity, the lower the iodide content in the outermost shell the greater the effects. Such an emulsion as EM-26 having a high iodide content (by not less than 10 mol%) in the outermost shell thereof is rather lower in sensitivity than that of the comparative emulsions.

<Example 4>

Table-17 similarly shows the effects of the grain size distribution.

In the invention, the sensitizing effects may effectively be obtained than in a monodispersed emulsion having a narrow grain size distribution.

The emulsions each having a broader distribution are inferior, in sharpness, to the emulsions having a narrower distribution. The monodispersed emulsions of the invention are more preferred to serve as an emulsion excellent in sensitivity, fog and sharpness.

<Example 5>

Table-18 also shows the effects of varying the volume of a highly iodide-containing shell.

The sensitizing effects of the invention is rather less when the volume of a highly iodide-containing shell is small, say 5%. (as in EM-33), though the emulsion may be sensitized a little, and the effects may be improved when using an emulsion provided with a highly iodide-containing shell having such a relatively greater volume as 12% in EM-32, 22% in EM-33 and 41% in EM-34.

<Example 6>

Table-19 further shows the effects of whole iodide content in the whole silver iodobromide.

In the invention, it is found that the emulsions each having a relatively higher whole iodide content, such as EM-35 and EM-36, show a reduced sensitizing effect; and that the emulsions each having a relatively lower whole iodide content, such as EM-38, are poor in graininess, sharpness and exposure range; and further that it is preferable to use the emulsions of the invention of which the iodide contents are within a suitable range, so that a high sensitivity, an excellent graininess, an excellent sharpness and a broad exposure range may be obtained.

Table 14
Example-1 (Effects of Intermediate shell)

Ex- No.	Ib mole	Ic mole	Id mole	Ie mole	If mole	Ig mole	Alh-Ih-Ia mole	All-Ia-Il mole	Whole con- tent of iodide %	Volume of each shell				Vari- ation co- effi- cient %	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range Alog ₂	Sharp- ness (MTF) %	Inter- layer sens- itivity
										Vh %	Va %	Vg %	Vf %							
Ex-5 (Other than Invention)	15	15	0.3	14.7	0	14.7	0	14.7	9.5	22	39	27	17	92	0.28	40	1.30	70	89	
Ex-6 (Other than Invention)	15	15	0.3	14.7	2	12.7	2	12.7	8.7	23	39	27	15	100	0.26	43	1.26	69	100	
Ex-7 (Invention)	15	10	0.3	14.7	5	9.7	5	9.7	7.5	22	39	27	12	163	0.24	38	1.30	73	178	
Ex-8 (Invention)	15	5	0.3	14.7	10	4.7	10	4.7	5.6	23	39	27	11	180	0.24	39	1.25	74	203	
Ex-9 (Other than Invention)	15	2	0.3	14.7	13	1.7	13	1.7	4.4	22	39	27	16	96	0.28	45	1.15	66	103	
Ex-9 (Other than Invention)	15	0.3	0.3	14.7	14.7	0	14.7	0	3.8	22	39	27	16	95	0.28	50	1.05	63	100	

Table 15
Example-1 (Effects of iodide contents of highly iodide-containing shells)

Ex-No.	Ih mole	If mole	Al-If-If mole	Al-If-If-If mole	Whole con- tent of iodide %	Volume of each shell			Veri- tion co- effi- cient %	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range Along %	Sharp- ness (MTF)	Inter- layer sensiti- vity
						Ih %	If %	Al-If-If %							
Ex-5 (Other than Invention)	15	0.3	14.7	0	9.5	22	39	27	17	92	0.28	40	1.30	70	89
Ex-9 (Other than Invention)	15	0.3	14.7	14.7	3.8	22	39	27	16	95	0.28	50	1.05	65	100
Ex-10 (Other than Invention)	5	5	4.7	0	3.4	22	39	27	10	90	0.24	52	1.96	66	92
Ex-11 (Invention)	8	5	7.7	3	4.1	23	39	27	10	117	0.24	45	1.10	72	115
Ex-12 (Invention)	10	5	9.7	5	4.5	23	39	27	11	165	0.24	47	1.16	69	175
Ex-4 (Invention)	15	5	14.7	10	5.6	22	39	27	11	180	0.24	39	1.25	74	205
Ex-13 (Invention)	20	5	19.7	15	6.7	22	39	27	12	170	0.24	40	1.30	75	180
Ex-14 (Invention)	30	5	25.7	25	8.8	22	39	27	13	160	0.26	38	1.32	78	175

Ex-ib.	Th mils	16 mils	At-Th-16 mils	At-Th-16 mils	Aff-16-17 mils	Whole ex- tent of iodide %	Volume of each shell			Veri- tion co- effi- cient %	Sensi- tivity	Fog	Craini- ness (R.A.S.)	Expo- sure range Along	Sharp- ness (RFP) %	Inter- layer sensiti- vity
							Vh %	Vm %	Vl %							
Ex 15 (Invention)	40	5	0.3	39.7	35	4.7	22	39	27	16	145	0.28	36	1.33	70	165
Ex 16 (Other than Invention)	40	0.3	0.3	39.7	39.7	0	22	39	27	19	95	0.30	41	1.26	68	98
Ex 17 (Invention)	50	5	0.3	49.7	45	4.7	22	39	27	35	110	0.35	46	1.28	66	112
Ex 18 (Other than Invention)	50	0.3	0.3	49.7	49.7	0	22	39	27	39	87	0.34	45	1.20	65	90

Table 16
Example-3 (Effects of iodide contents of low iodide-containing shells and intermediate shells)

EM-No.	Ia mole %	Ib mole %	Ic mole %	Al-Ib-Ic mole %	Al-Ib-Ic mole %	Whole content of iodide %	Volume of each shell			Veri- fication co- effi- cient %	Sens- itivity	Fog	Graini- ness (R.M.S.)	Expo- sure range AlogB	Sharp- ness (MPP) %	Inter- layer sens- itivity
							Va %	Vb %	Vc %							
EM-3 (Other than Invention)	15	15	0.5	14.7	0	9.5	22	39	27	17	92	0.28	40	1.30	70	89
EM-9 (Other than Invention)	15	0.5	0.5	14.7	14.7	9.8	22	39	27	16	95	0.28	50	1.05	65	100
EM-19 (Invention)	15	5	0	15	10	5.5	22	39	27	10	175	0.24	38	1.32	73	190
EM-4 (Invention)	15	5	0.5	14.7	10	5.6	22	39	27	11	180	0.24	39	1.25	74	203
EM-20 (Invention)	15	5	0.5	14.5	10	5.7	22	39	27	11	181	0.24	41	1.28	75	210
EM-21 (Invention)	15	5	1.5	13.5	10	5.9	22	39	27	11	130	0.24	38	1.30	77	214
EM-23 (Other than Invention)	15	5	4.5	10.5	10	6.7	22	39	27	11	95	0.24	47	1.30	78	55
EM-7 (Invention)	15	10	0.5	14.7	5	7.5	22	39	27	12	163	0.24	38	1.30	75	198

Ex-No.	In mols	I ₂ mols	I ₁ mols	Al-th-II mols	Al-th-III mols	Al ₂ -I ₂ -II mols	Whole con- tent of iodide %	Volume of each shell			Veri- tation co- effi- cient %	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range AlogE	Sharp- ness (MTF) %	Inter- layer sensi- tivity
								V _h %	V _m %	V _l %							
Ex-6 (Other than Invention)	15	15	0.3	14.7	2	12.7	8.7	22	39	27	15	100	0.26	42	1.30	69	100
Ex-23 (Invention)	15	10	1.3	13.5	5	8.5	7.9	22	39	27	13	155	0.24	40	1.28	74	145
Ex-24 (Invention)	15	10	4.5	10.5	5	5.5	8.7	22	39	27	13	120	0.24	45	1.30	75	118
Ex-25 (Other than Invention)	15	10	8	7	5	2	9.6	22	39	27	12	68	0.24	49	1.32	75	38
Ex-26 (Other than Invention)	25	17	11	14	8	6	15.3	22	39	27	13	45	0.26	51	1.31	78	40

Table 17
Example-4 (Effects of grain size distribution)

Ex- No.	Ih mole	Ii mole	Ij mole	Al- Ih-Ij mole	Al- Ih-Ij mole	Al- Ih-Ij mole	Whole con- tent of iodide %	Volume of each shell			Veri- tion co- effi- cient %	Sensi- tivity	Fog	Graini- ness (B.M.S.)	Expo- sure range Alog ₂	Sharp- ness (M37)	Inter- layer sensi- tivity
								Ih %	Ii %	Ij %							
Ex-3 (Other than Invention)	15	15	0.3	14.7	0	14.7	9.5	22	39	27	17	92	0.28	40	1.20	70	89
Ex-9 (Other than Invention)	15	0.3	0.3	14.7	14.7	0	3.8	22	39	27	16	95	0.28	50	1.09	63	100
Ex-4 (Invention)	15	5	0.3	14.7	10	4.7	5.6	22	39	27	11	180	0.24	39	1.25	74	203
Ex-27 (Invention)	15	5	0.3	14.7	10	4.7	5.6	22	39	27	9	190	0.22	38	1.28	75	210
Ex-28 (Invention)	15	5	0.3	14.7	10	4.7	5.6	22	39	27	18	180	0.28	36	1.32	68	195
Ex-29 (Other than Invention)	15	0.3	0.3	14.7	14.7	0	3.8	22	39	27	19	101	0.30	55	0.95	63	98
Ex-30 (Invention)	15	5	0.3	14.7	10	4.7	5.6	22	39	27	32	152	0.42	42	1.30	66	164
Ex-31 (Other than Invention)	15	0.3	0.3	14.7	14.7	0	3.8	22	39	27	34	116	0.38	48	1.01	60	95

Ph. No.	1h mil's	1m mil's	1f mil's	1h-1h-1f mil's	1h-1h-1m mil's	1f-1m-1f mil's	Waic cont of iodine %	Volume of each shell			Vari- tion co- effi- cient	Sensi- tivity	Fog	Grain- ness (h.M.S.)	Expo- sure range Alog ₂	Sharp- ness (MIP) %	Inter- layer sensit- ivity
89-15 (Invent.)	40	5	0.3	30.7	35	4.7	11.1	Vh %	Vm %	Vf %	18	145	0.28	36	1.33	70	165
89-17 (Invent.)	50	5	0.3	49.7	45	4.7	12.2	22	39	27	33	110	0.33	46	1.28	66	112

A-1

5 10 15 20 25 30 35 40 45 50 55

Table 18
Example-3 (Effects of volume of highly iodide-containing shells)

Ex-No.	In mole	I ₂ mole	Al-III-III mole	Al-III-III-III mole	Al-III-III-III-III mole	Whole con- tent of iodides %	Volume of each shell			Veri- fication co- effi- cient %	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range Along %	Sharp- ness (mm)	Inter- layer sensi- tivity	
							V _h %	V _m %	V _w %								
Ex-3 (Other than Invention)	15	15	0.3	14.7	0	14.7	9.5	22	39	27	17	92	0.28	40	1.30	70	89
Ex-3 (Other than Invention)	15	0.3	0.3	14.7	14.7	0	9.8	22	39	27	16	93	0.28	50	1.05	63	100
Ex-4 (Invention)	15	5	0.3	14.7	10	4.7	5.6	22	39	27	11	180	0.24	39	1.25	74	203
Ex-32 (Invention)	15	5	0.3	14.7	10	4.7	4.6	12	49	27	10	165	0.24	45	1.10	70	185
Ex-33 (Invention)	15	5	0.3	14.7	10	4.7	4.0	5	56	27	10	115	0.24	44	1.08	68	138
Ex-34 (Invention)	15	5	0.3	14.7	10	4.7	7.6	41	20	27	12	132	0.24	33	1.35	76	164

55

50

45

40

35

30

25

20

15

10

5

Table 19
Example-6 (Effects of an aggregate iodide content)

EM-No.	Ib mols	Ia mols	I ₂ mols	Al-Ib-I ₂ mols	Al-Ib-I ₂ -Ia mols	Whole con- tent of iodide %	Volume of each shell			Veri- tion co- effi- cient %	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range Alog ₂ %	Sharp- ness (MDF) %	Inter- layer sensi- tivity
							Vb %	Va %	V ₂ %							
EM-3 (Other than Invention)	15	15	0.3	14.7	0	9.5	22	39	27	17	92	0.28	40	1.32	70	89
EM-9 (Other than Invention)	15	0.3	0.3	14.7	14.7	3.8	22	39	27	16	95	0.28	50	1.05	63	100
EM-4 (Invention)	15	5	0.3	14.7	10	5.6	22	39	27	11	180	0.24	39	1.23	74	205
EM-35 (Invention)	25	10	5	20	15	11	22	39	27	12	192	0.24	55	1.32	75	118
EM-36 (Invention)	35	10	5	30	25	13.7	22	39	27	14	116	0.26	60	1.28	70	107
EM-37 (Other than Invention)	35	7.5	5	30	27.5	12.2	22	39	27	13	70	0.26	65	1.32	70	95
EM-33 (Invention)	15	5	0.3	14.7	10	4.0	5	56	27	10	180	0.24	45	1.10	68	135

Ex- No.	Ih mols	Is mols	Al-Is-II mols	Alh-Is-Is mols	Alh-Is-Is mols	Whole con- tent of iodide %	Volume of each shell			Veri- tion co- effi- cient	Sensi- tivity	Fog	Graini- ness (R.M.S.)	Expo- sure range Along	Sharp- ness (MPP)	Inter- layer sensi- tivity
							Vh	Vm	Vl							
Ex-38 (Invention)	8	4	0.3	7.7	4	3.7	5	56	27	9	105	0.23	63	0.90	63	105
Ex-39 (Other than Invention)	8	0.3	0.3	7.7	7.7	0	5	56	27	11	80	0.24	70	0.93	62	75

Claims

1. A negative type silver halide photographic material comprising silver halide grains of core-shell structure which consists of an inner core essentially consisting of silver bromide or silver iodobromide and a plurality of shells, essentially consisting of silver bromide or silver iodobromide, wherein said

- silver halide grains comprise (a) an outermost shell containing from 0 to 10 mol% silver iodide, (b) a highly iodide-containing shell provided inside said outermost shell, of which the silver iodide content is from 6 to 40 mol% and is at least 6 mol% higher than that of said outermost shell, and (c) an intermediate shell provided between the shells (a) and (b) the silver iodide content of said intermediate shell being at least 3 mol% higher than that of said outermost shell, and at least 3 mol% lower than that of said high iodide-containing shell.
2. The silver halide photographic material according to claim 1, wherein the silver iodide content of said highly iodide containing-shell is from 10 to 40 mol%.
 3. The silver halide photographic material according to claim 1 or 2 wherein the silver iodide content of said outermost shell is from 0 to 3 mol%.
 4. The silver halide photographic material according to claim 3, wherein the silver iodide content of said outermost shell is from 0 to 2 mol%.
 5. The silver halide photographic material according to claim 4, wherein the silver iodide content of said outermost shell is from 0 to 1 mol%.
 6. The silver halide photographic material according to any one of claims 1 to 5, wherein the difference of in silver iodide content between the intermediate shell and the outermost shell is from 4 to 35 mol%.
 7. The silver halide photographic material according to any one of claims 1 to 6 wherein the difference in the silver iodide content between the highly iodide-containing shell and the intermediate shell is from 4 to 35 mol%.
 8. The silver halide photographic material according to any one of claims 1 to 7 wherein the difference in the silver iodide content between the highly iodide-containing shell and the outermost shell is not less than 8 mol%.
 9. The silver halide photographic material according to claim 8, wherein the difference of the silver iodide content between the highly iodide-containing shell and the outermost shell is not less than 10 mol%.
 10. The silver halide photographic material according to any one of claims 1 to 9, wherein the silver iodide content of the inner core is from 0 to 40 mol%.
 11. The silver halide photographic material according to claim 10, wherein the silver iodide content of the inner core is from 0 to 10 mol%.
 12. The silver halide photographic material according to claim 11, wherein the silver iodide content of the inner core is from 0 to 6 mol%.
 13. The silver halide photographic material according to any one of claims 1 to 12, wherein the volume of the outermost shell is from 4 to 70% of the whole volume of the silver halide grain.
 14. The silver halide photographic material according to claim 13, wherein the volume of the outermost shell is from 10 to 50% of the whole volume of silver halide grain.
 15. The silver halide photographic material according to any one of claims 1 to 14 wherein the volume of the highly iodide-containing shell is from 10 to 80% of the whole volume of the silver halide grain.
 16. The silver halide photographic material according to claim 15, wherein the volume of the highly iodide-containing shell is from 20 to 50% of the whole volume of the silver halide grain.
 17. The silver halide photographic material according to claim 16, wherein the volume of the highly iodide-containing shell is from 20 to 45% of the whole volume of the silver halide grain.
 18. The silver halide photographic material according to any one of claims 1 to 17, wherein the volume of

the intermediate shell is from 5 to 60% of the whole volume of the silver halide grain.

19. The silver halide photographic material according to claim 18, wherein the volume of the intermediate shell is from 20 to 55% of the whole volume of the silver halide grain.
20. The silver halide photographic material according to any one of claims 1 to 19, wherein the size of the inner core is from 0.05 to 0.8 μm .
21. The silver halide photographic material according to claim 20, wherein the size of the inner core is from 0.05 to 0.4 μm .
22. The silver halide photographic material according to any one of claims 1 to 21, wherein the whole content of silver iodide of the silver halide grain is from 1 to 20 mol%.
23. The silver halide photographic material according to claim 22, wherein the whole content of silver iodide of the silver halide grain is from 1 to 15 mol%.
24. The silver halide photographic material according to claim 23, wherein the whole content of silver iodide of the silver halide grain is from 2 to 12 mol%.
25. The silver halide photographic material according to any one of claims 1 to 24, wherein the silver halide grains are monodispersed.
26. The silver halide photographic material according to claim 25, wherein the variation coefficient of dispersion of the silver halide grains is not more than 20%.
27. The silver halide photographic material according to claim 26, wherein the variation coefficient is not more than 15%.

30 Revendications

1. Matériau photographique à l'halogénure d'argent de type négatif comprenant des grains d'halogénure d'argent à structure de coque de noyau, laquelle consiste en un noyau interne consistant essentiellement en bromure d'argent ou en iodobromure d'argent et en une pluralité de coques, consistant essentiellement en bromure d'argent ou en iodobromure d'argent, dans lequel lesdits grains d'halogénure d'argent comprennent (a) une coque externe contenant de 0 à 10 moles % d'iodure d'argent, (b) une coque à haute teneur en iodure prévue à l'intérieur de ladite coque externe, dont la teneur en iodure d'argent est de 6 à 40 moles % et est au moins 6 moles % supérieure à celle de ladite coque externe, et (c) une coque intermédiaire prévue entre les coques (a) et (b), la teneur en iodure d'argent de ladite coque intermédiaire étant au moins 3 moles % supérieure à celle de la coque externe, et au moins 3 moles % inférieure à celle de ladite coque à haute teneur en iodure.
2. Matériau photographique à l'halogénure d'argent selon la revendication 1, dans lequel la teneur en iodure d'argent de la coque à haute teneur en iodure est de 10 à 40 moles %.
3. Matériau photographique à l'halogénure d'argent selon la revendication 1 ou 2, dans lequel la teneur en iodure d'argent de ladite coque externe est de 0 à 3 moles %.
4. Matériau photographique à l'halogénure d'argent selon la revendication 3, dans lequel la teneur en iodure d'argent de ladite coque externe est de 0 à 2 moles %.
5. Matériau photographique à l'halogénure d'argent selon la revendication 4, dans lequel la teneur en iodure d'argent de ladite coque externe est de 0 à 1 mole %.
6. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 5, dans lequel la différence de teneur en iodure d'argent entre la coque intermédiaire et la coque externe est de 5 à 35 moles %.

7. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 6, dans lequel la différence entre la teneur en iodure d'argent entre la coque à haute teneur en iodure et la coque intermédiaire est de 4 à 35 moles %.
- 5 8. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 7, dans lequel la différence de teneur d'iodure d'argent entre la coque à haute teneur en iodure et la coque externe n'est pas inférieure à 8 moles %.
9. Matériau photographique à l'halogénure d'argent selon la revendication 8, dans lequel la différence de teneur en iodure d'argent entre la coque à haute teneur en iodure et la coque externe n'est pas inférieure à 10 moles %.
- 10 10. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 9, dans lequel la teneur en iodure d'argent du noyau interne est de 0 à 40 moles %.
- 15 11. Matériau photographique à l'halogénure d'argent selon la revendication 10, dans lequel la teneur en iodure d'argent du noyau interne est de 0 à 10 moles %.
12. Matériau photographique à l'halogénure d'argent selon la revendication 11, dans lequel la teneur en iodure d'argent du noyau interne est de 0 à 6 moles %.
- 20 13. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 12, dans lequel le volume de la coque externe est de 4 à 70 % du volume total du grain d'halogénure d'argent.
- 25 14. Matériau photographique à l'halogénure d'argent selon la revendication 13, dans lequel le volume de la coque externe est de 10 à 50 % du volume total du grain d'halogénure d'argent.
- 30 15. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications 1 à 14, dans lequel le volume de la coque à haute teneur en iodure est de 10 à 80 % du volume total du grain d'halogénure d'argent.
- 35 16. Matériau photographique à l'halogénure d'argent selon la revendication 15, dans lequel le volume de la coque à haute teneur en iodure est de 20 à 50 % du volume total du grain d'halogénure d'argent.
17. Matériau photographique à l'halogénure d'argent selon la revendication 16, dans lequel le volume de la coque à haute teneur en iodure est de 20 à 45 % du volume total du grain d'halogénure d'argent.
- 40 18. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications de 1 à 17, dans lequel le volume de la coque intermédiaire est de 5 à 60 % du volume total du grain d'halogénure d'argent.
19. Matériau photographique à l'halogénure d'argent selon la revendication 18, dans lequel le volume de la coque intermédiaire est de 20 à 55 % du volume total du grain d'halogénure d'argent.
- 45 20. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications de 1 à 19, dans lequel la taille du noyau interne est de 0,05 à 0,8 μm .
- 50 21. Matériau photographique à l'halogénure d'argent selon la revendication 20, dans lequel la taille du noyau interne est de 0,05 à 0,4 μm .
22. Matériau photographique à l'halogénure d'argent selon l'une quelconque des revendications de 1 à 21, dans lequel la teneur totale en iodure d'argent du grain d'halogénure d'argent est de 1 à 20 moles %.
- 55 23. Matériau photographique à l'halogénure d'argent selon la revendication 22, dans lequel la teneur totale en iodure d'argent du grain d'halogénure d'argent est de 1 à 15 moles %.
24. Matériau photographique à l'halogénure d'argent selon la revendication 23, dans lequel la teneur totale

en iodure d'argent du grain d'halogénure d'argent est de 2 à 12 moles %.

25. Matériau photographique à l'halogénure d'argent selon l'une des revendications de 1 à 24, dans lequel les grains d'halogénure d'argent sont monodispersés.
26. Matériau photographique à l'halogénure d'argent selon la revendication 25, dans lequel le coefficient de variation de la dispersion des grains d'halogénure d'argent n'est pas supérieur à 20 %.
27. Matériau photographique à l'halogénure d'argent selon la revendication 26, dans lequel le coefficient de variation n'est pas supérieur à 15 %.

Patentansprüche

1. Photographisches Silberhalogenid-Negativmaterial mit Silberhalogenidkörnchen mit Kern-Hülle-Struktur, bestehend aus einem inneren Kern im wesentlichen aus Silberbromid oder Silberjodbromid und einer Mehrzahl von Hüllen im wesentlichen aus Silberbromid oder Silberjodbromid, wobei die Silberhalogenidkörnchen
 - (a) eine äußerste Hülle mit 0 - 10 Mol-% Silberjodid,
 - (b) eine unter der äußersten Hülle vorgesehene und einen hohen Jodidgehalt aufweisende Hülle, deren Silberjodidgehalt 6 - 40 Mol-% beträgt und mindestens 6 Mol-% höher ist als derjenige der äußersten Hülle, und
 - (c) eine zwischen den Hüllen (a) und (b) vorgesehene Zwischenhülle, deren Silberjodidgehalt mindestens 3 Mol-% höher ist als derjenige der äußersten Hülle und mindestens 3 Mol-% niedriger ist als derjenige der einen hohen Jodidgehalt aufweisenden Hülle,
 umfaßt.
2. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß der Silberjodidgehalt der einen hohen Jodidgehalt aufweisenden Hülle 10 - 40 Mol-% beträgt.
3. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Silberjodidgehalt der äußersten Hülle 0 - 3 Mol-% beträgt.
4. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 3, dadurch gekennzeichnet, daß der Silberjodidgehalt der äußersten Hülle 0 - 2 Mol-% beträgt.
5. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 4, dadurch gekennzeichnet, daß der Silberjodidgehalt der äußersten Hülle 0 - 1 Mol-% beträgt.
6. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der Unterschied im Silberjodidgehalt zwischen der Zwischenhülle und der äußersten Hülle 4 - 35 Mol-% beträgt.
7. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Unterschied im Silberjodidgehalt zwischen der einen hohen Jodidgehalt aufweisenden Hülle und der Zwischenhülle 4 - 35 Mol-% beträgt.
8. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Unterschied im Silberjodidgehalt zwischen der einen hohen Jodidgehalt aufweisenden Hülle und der äußersten Hülle nicht weniger als 8 Mol-% beträgt.
9. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 8, dadurch gekennzeichnet, daß der Unterschied im Silberjodidgehalt zwischen der einen hohen Jodidgehalt aufweisenden Hülle und der äußersten Hülle nicht weniger als 10 Mol-% beträgt.
10. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß der Silberjodidgehalt des inneren Kerns 0 - 40 Mol-% beträgt.
11. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 10, dadurch gekennzeichnet,

daß der Silberjodidgehalt des inneren Korns 0 - 10 Mol-% beträgt.

12. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 11, dadurch gekennzeichnet, daß der Silberjodidgehalt des inneren Korns 0 - 6 Mol-% beträgt.
- 5 13. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß das Volumen der äußersten Hülle 4 - 70% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 10 14. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 13, dadurch gekennzeichnet, daß das Volumen der äußersten Hülle 10 - 50% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 15 15. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß das Volumen der einen hohen Jodigehalt aufweisenden Hülle 10 - 80% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 20 16. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 15, dadurch gekennzeichnet, daß das Volumen der einen hohen Jodidgehalt aufweisenden Hülle 20 - 50% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 25 17. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 16, dadurch gekennzeichnet, daß das Volumen der einen hohen Jodidgehalt aufweisenden Hülle 20 - 45% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 30 18. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 17, dadurch gekennzeichnet, daß das Volumen der Zwischenhülle 5 - 60% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
- 35 19. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 18, dadurch gekennzeichnet, daß das Volumen der Zwischenhülle 20 - 55% des Gesamtvolumens des Silberhalogenidkörnchens beträgt.
20. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 19, dadurch gekennzeichnet, daß die Größe des inneren Korns 0,05 - 0,8 μm beträgt.
21. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 20, dadurch gekennzeichnet, daß die Größe des inneren Korns 0,05 - 0,4 μm beträgt.
- 40 22. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 21, dadurch gekennzeichnet, daß der Gesamtgehalt an Silberjodid in dem Silberhalogenidkörnchen 1 - 20 Mol-% beträgt.
- 45 23. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 22, dadurch gekennzeichnet, daß der Gesamtgehalt an Silberjodid des Silberhalogenidkörnchens 1 - 15 Mol-% beträgt.
24. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 23, dadurch gekennzeichnet, daß der Gesamtgehalt an Silberjodid des Silberhalogenidkörnchens 2 - 12 Mol-% beträgt.
- 50 25. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach einem der Ansprüche 1 bis 24, dadurch gekennzeichnet, daß es sich bei den Silberhalogenidkörnchen um monodisperse Silberhalogenidkörnchen handelt.
- 55 26. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 25, dadurch gekennzeichnet, daß die prozentuale quadratische Streuung der Silberhalogenidkörnchendispersion nicht mehr als 20% beträgt.
27. Photographisches Silberhalogenid-Aufzeichnungsmaterial nach Anspruch 26, dadurch gekennzeichnet,

daß die prozentuale quadratische Streuung nicht mehr als 15% beträgt.

5

10

15

20

25

30

35

40

45

50

55